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Project No./(Center No.) E-18-630 (R6248-0A0) GTRC DATE 1 / 5 / 87

Project Director: R. Hochman School Material Engineering

Sponsor: IBM Corporation

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Funded:	$	$ 30,000

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Title: A Survey of Ion Plating Processes

ADMINISTRATIVE DATA — OCA Contact John B. Schonk ext. 4820

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NOTICE OF PROJECT CLOSEOUT

Date 5/5/89

Project No. E-18-630 Center No. R6248-0A0

Project Director R. F. Hockman School/Lab Mat. Eng.

Sponsor IBM Corporation

Contract/Grant No. 6045 - Mod Z434900-U65 GTRC XX GIT ____

Prime Contract No. ____

Title A Survey of Ion Plating Processes

Effective Completion Date 12/31/87 (Performance) 12/31/87 (Reports)

Closeout Actions Required:

____ None
X Final Invoice or Copy of Last Invoice
____ Final Report of Inventions and/or Subcontracts - Patent questionnaire sent to P/I.
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____ Classified Material Certificate
____ Release and Assignment
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Includes Subproject No(s). ____

Subproject Under Main Project No. ____

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Georgia Institute of Technology
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August 6, 1987

MEMORANDUM REPORT

TO: Dr. E. J. Lee
IBM, Systems Technology Division Laboratory

FROM: Dr. Robert F. Hochman
Metallurgy Program
Georgia Institute of Technology

SUBJECT: Ion Plating Technology Assessment Program

I. ION PLATING SYSTEMS STUDY

In ion plating a wide range of variables affect operation of the process and dictate the characteristics of the coating. In work we have previously performed, it has been clearly shown that two factors greatly influence the coating operation and the resultant properties of the coating, these are: the cleanliness of the system and the temperature of the substrate. However, work in the intervening months since the end of the second year on this project has shown the added importance of the ionization factor in this type of deposition. In diode ion plating, the ionization efficiency reported is in the neighborhood of 0.5 to 1.0 per cent. As one would expect, in straight vacuum deposition and for sputtering the ionization is much lower.

Our research on the hollow cathode ion plating system, and more recently on a triode system has shown that the ionization efficiency can easily reach 5% and in some cases be as high as

10%. The ionization efficiency is particularly important when one considers working with various reactive ion plating processes. This was clearly shown in the work of Hochman and Erdemir[1] where indeed the normal substrate temperatures necessary to achieve the various types of coating morphology has markedly changed when the higher ionization hollow cathode deposition (HCD) process is used for plating titanium nitride. A simple plot showing the Movchan and Demchishin, and the Thornton temperature vs. morphology and our work using hollow cathode deposition shows that indeed a fine grain sized, equiaxed structure can be achieved as low as .25 of the melting point. This is shown in Figure 1. This is remarkably lower than the .5 of the melting point required for the lower ionization processes.

In addition to lower substrate temperature, another very interesting phenomena was observed in the interactive zone (substrate to film) for the higher ionization processes. The interactive zone in HCD ion plating of several species has shown several hundred angstroms depth to the interface region resulting from intermix of the substrate and the coating. Thus, this very important consideration, a broad interface gradient, results in higher coating adhesion. Again, this is an effect of the higher ionization efficiency. Figure 2 shows the evidence of this adhesion for titanium nitride in a relatively simple system of coating on a high strength bearing steel.

The first stage of this program year has been focused on ionization effects on interface phenomena and the ionization

effect in different systems (with different ionization efficiency) on reactive ion coatings. Triode ion plating, where a thermionic emitter has been added to increase ionization efficiency, has been one of the main studies in this survey program since the ionization efficiency can be varied as well as increased in this type of system.

II. DEVELOPMENT OF THERMIONICALLY ASSISTED TRIODE ION PLATING

These results indicate further improvement of the coating properties can be achieved if ionization efficiencies are increased. A versatile means of achieving high ionization levels is to use a thermionically assisted triode system (TATIP). In such a system a positive electrode and a thermionic source are utilized in conjunction with a conventional diode ion plating system. It is desirable to attain high current densities while keeping the gas pressure low to reduce gas scattering and the possibility for contamination. By utilizing the TATIP technique, one can supply additional electrons through thermionic emission. These electrons will be attracted by the positively bias probe with the result of increased ionization efficiency.

In normal ion plating, a large amount of thermal energy is brought to substrate and the surface temperature of the substrate may be high enough to change the heat treat microstructure of the specimen (e.g., surface softening of the peak hardened steel). Reducing the pressure of inert gas in the system can minimize the surface heating effect and it can also decrease the contamination inside the system. However, in an ion

plating system as the pressure of the self-sustained glow discharge is reduced, the number of ionization collisions per unit length made by electrons leaving the cathode diminishes and the ion density in the glow discharge is also reduced. In order to support a glow discharge at low pressure or attain higher ionization efficiency in the self-sustained glow discharge, it is necessary to provide additional electrons by the use of a hot filament which emits electrons through thermionic emission. An additional electrode plate added to the system draws the full emission current from the thermionic cathode when a small positive voltage is applied to it. A schematic illustration of the thermionically assisted triode ion plating apparatus we have constructed is shown in Figure 3.

In our system, the thermionic cathode is a heated tungsten filament capable of tolerating ion bombardment for a long period. The tungsten filament was supported by a medium current, ceramic insulated solid OFHC conductor electric feedthrough fabricated by MDC Vacuum Products Corporation, Model MC-152. Extra copper wires were used to ensure that the filament was positioned close to the chromium evaporation wire and an AC power supply (Powerstat Variable Autotransformer, supplied by the Superior Electric Co.) was used to heat up the thermionic filament.

The positive electrode plate was designed not only to increase the ionization efficiency in the argon glow discharge, but also to make the best use of the source material. Essentially, the positive electrode was an evaporation source

shield which stops the emission of source particles in directions other than that to the specimen. The shield was electrically connected to a DC power supply (Sorensen Power Supplies, Model DCR 300-18A) outside the vacuum system through an electrical feedthrough supplied by MDC Vacuum Products Corporation, Model MC-150. An alumina plate was utilized to separate this positively biased shield from the grounded vacuum base plate.

Following check-out of the system, Cr is to be used as the initial test source material and the results of initial tests will be available in the next report.

Fully submitted,

Dr. Robert F. Hochman
Professor
School of Materials Engineering

RFH:ew

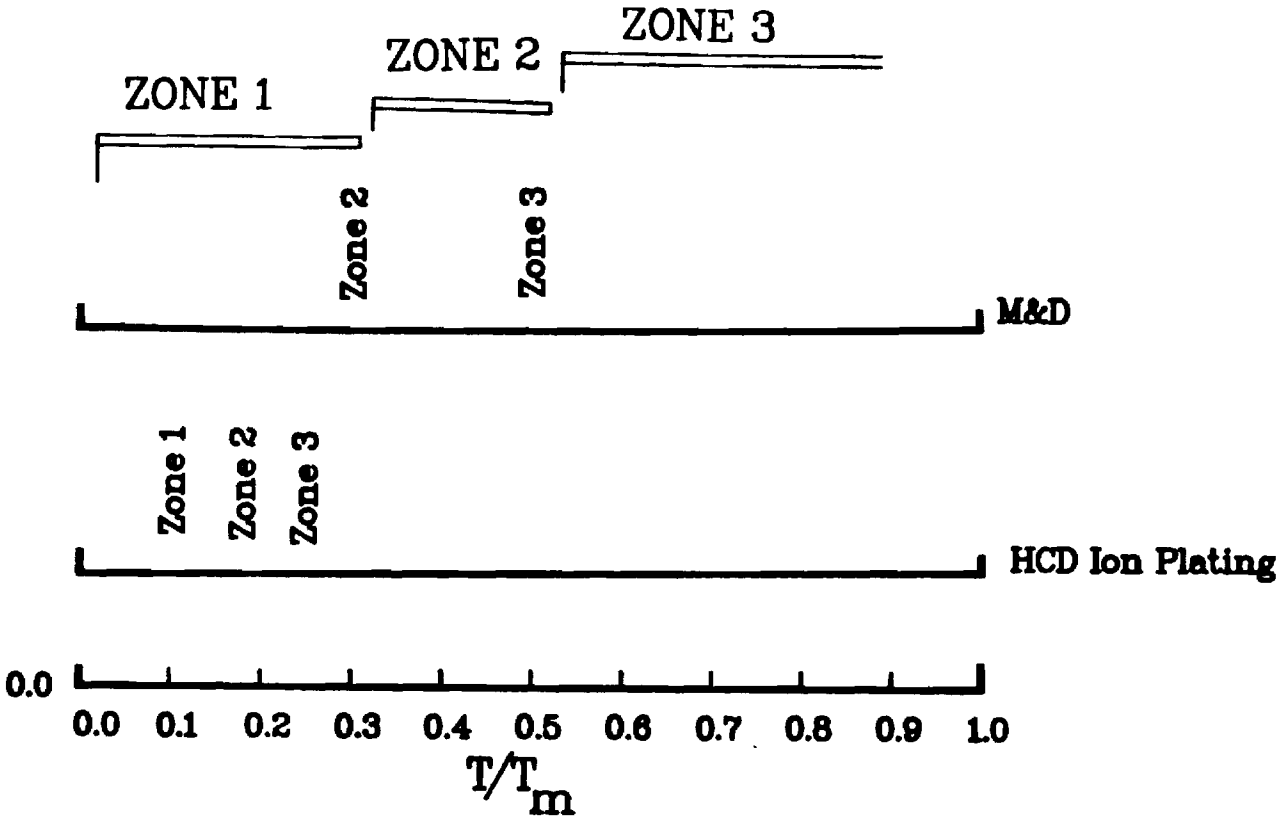

Figure 1. Zone Morphologies for TiN Using HCD Ion Plating Compared With the PVD Morphologies Expected for TiN According to Movchan and Demchishin's Model.

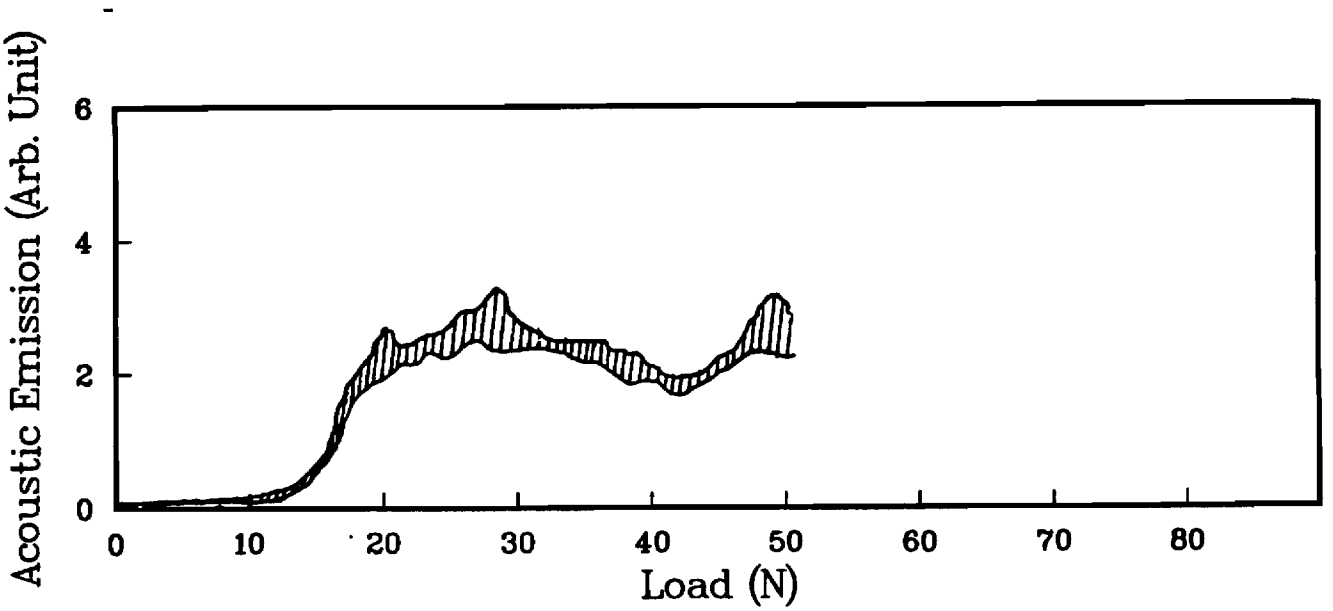

Figure 2. An AE-load Diagram of an (HCD) Ion Plated TiN Film Plated at 300°C on M50 Steel. Note the AE Emission Starts at Approximately 3x's Normal Plated TiN.

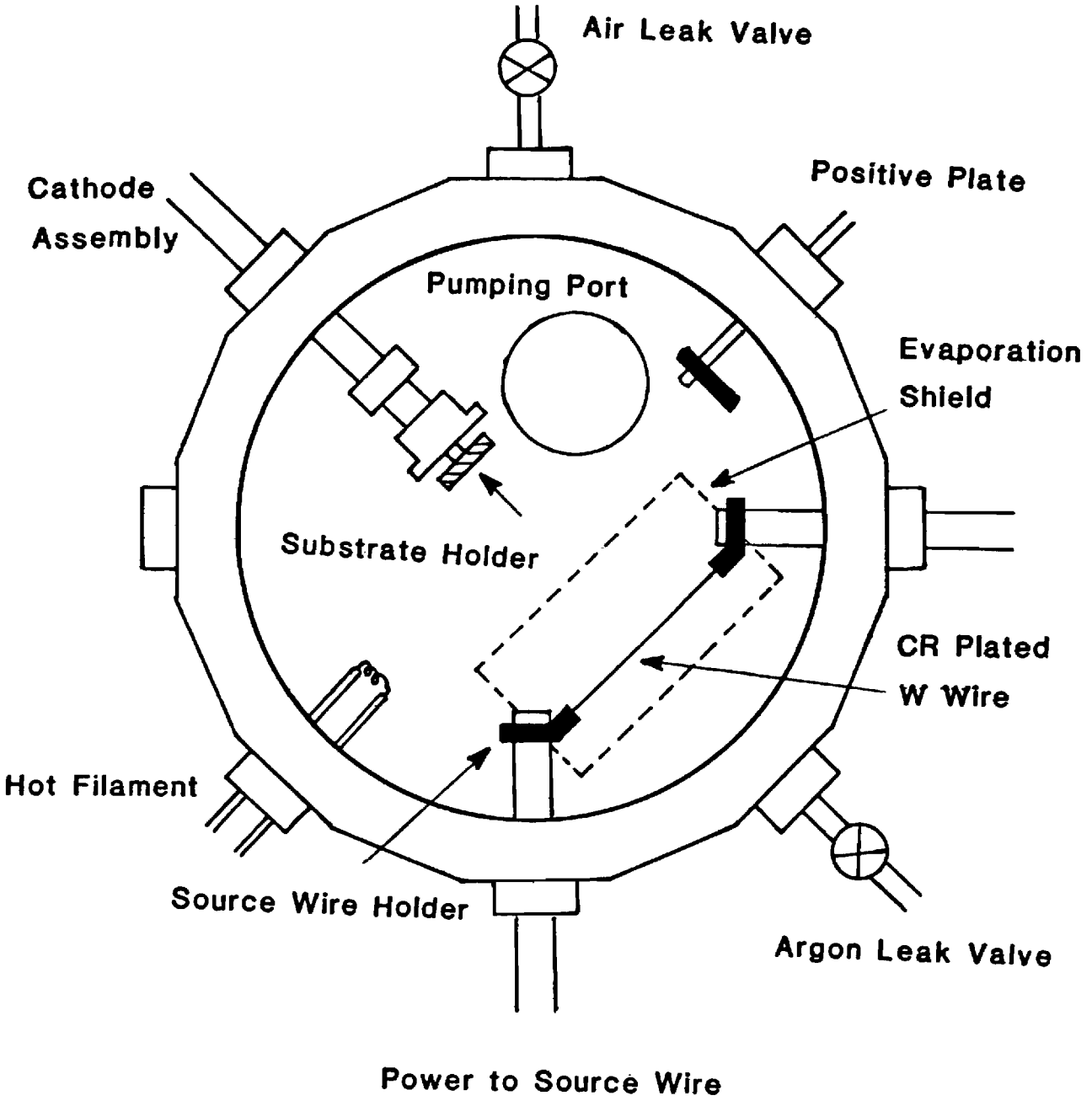

Figure 3. A Schematic Illustration of the Horizontal Type TATIP Apparatus Inside the Vacuum Chamber.

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January 20, 1988

MEMORANDUM REPORT

TO: Dr. E. J. Lee
IBM, Systems Technology Division Laboratory

FROM: Dr. Robert F. Hochman
Metallurgy Program
Georgia Institute of Technology

SUBJECT: Ion Plating Technology Assessment Program

I. EVALUATION OF DISCHARGE CURRENT - BIAS VOLTAGE RELATIONSHIPS FOR THE THERMIONIC ASSISTED TRIODE ION PLATING SYSTEM

The system used in this study was described in previous report. The characteristics of this system, in a pure argon glow discharge is shown in Figures 1 through 6, where the discharge currents detected on the cathode are plotted as a function of applied negative bias voltage. The cathode bias voltage varies from 0 KV to -4 KV. During these experiments, the system was back filled with pure argon to a level of 20 microns for the results shown in Figures 1 and 2 and 5 microns for the results shown in Figures 3 and 4. The thermionic filament was either off (0 Amp) or on (18 Amp AC) in these experiments. This was done to examine the effects of vacuum level and thermionic electron emission on the discharge current. In each plot, the bias voltage applied to the positive probe was varied from 0 V to +100 V. The surface area of the cathode was 32 cm^2.

The application of positive bias voltage to the probe can significantly increase the discharge currents even when thermionic filament was not turned on. For example, when argon pressure is 20 microns and cathode bias is -3 KV, the discharge current increases from 20 mA to 25 mA if the probe is biased at +100 V. The supply of thermionic electrons alone to the glow discharge can also enhance the discharge. However, the best result in terms of the discharge current attainable is obtained when both the positive probe and the thermionic filament are employed. As in the case where the argon pressure is 20 microns and cathode bias is -3 KV, the discharge current increases from 20 mA to 38 mA when 18 Amp (AC) and +100 V are applied to the thermionic filament and the positive probe; respectively. At lower argon pressure (5 micron), these same experimental parameters can increase the discharge current from 5 mA to 19 mA. It should be noted that the combination of thermionic filament and positive probe becomes more effective with the increase of cathode bias voltage. The comparison between the performance of this system in diode mode and thermionically assisted triode mode for the two different vacuum levels are shown in Figures 5 and 6.

It was also found that the discharge current density decreased when chromium was vaporized and emitted into the glow discharge. This may be related to the neutral concentration in the Cr as it comes from the evaporation source.

II. EVALUATION OF VARIATION IN CATHODE TEMPERATURE AND CURRENT

In the sputtering of the work piece (or cathode), much of

the energy is brought to the piece by ions and energetic neutral particles. The bulk temperature of the cathode was recorded when the cathode was biased at -3 KV and -2 KV. Argon pressure was dynamically maintained at 20 microns. The results are shown in Figures 7 and 8. The effect of passing cooling water through the cathode assembly on its bulk temperature was examined. When the cooling system was not used, the initial heating rate of the bulk cathode for -3 KV bias (72 degrees C/min.) was higher than that of -2 KV bias (28 degrees C/min.). After 30 minutes both heating curves begin to level off. The bulk temperatures detected then were 215 degrees C (-3 KV) and 126.5 degrees (-2 KV). If the cooling system was turned on, the bulk temperatures for both voltage levels remained at low values, e.g., -36.5 degrees C for -3 KV and 29.5 degrees C for -2 KV measured after 60 minutes of sputtering well after the temperature appeared to stabilize. The temperature on the top surface of the cathode, where the energetic particles are incident will be the subject of a calculation to be reported later.

Prior to sputtering, the surface of the cathode was covered with oxide together with other contaminants. At the beginning of sputtering, a higher cathode current was observed because of the surface contaminants as shown in Figure 8. As these contaminants were gradually removed from the surface, the cathode current decreased to a low stable value depending on the cathode bias voltage. A higher limiting current density (0.60 A/cm sq.) was obtained at high bias (-3 KV) than occurred at lower bias (e.g.,

0.338 A/cm^2 for -2 KV).

III. Continuation Studies

A calculation of cathode surface temperature, based on the bulk temperature determinations and the other parameter measured for the system, will be made. Preliminary studies of Cr film properties have also been made and more detailed and precise characterization of Cr film properties in relation to the TATIP system will be presented in the final report, as will the surface temperature calculations.

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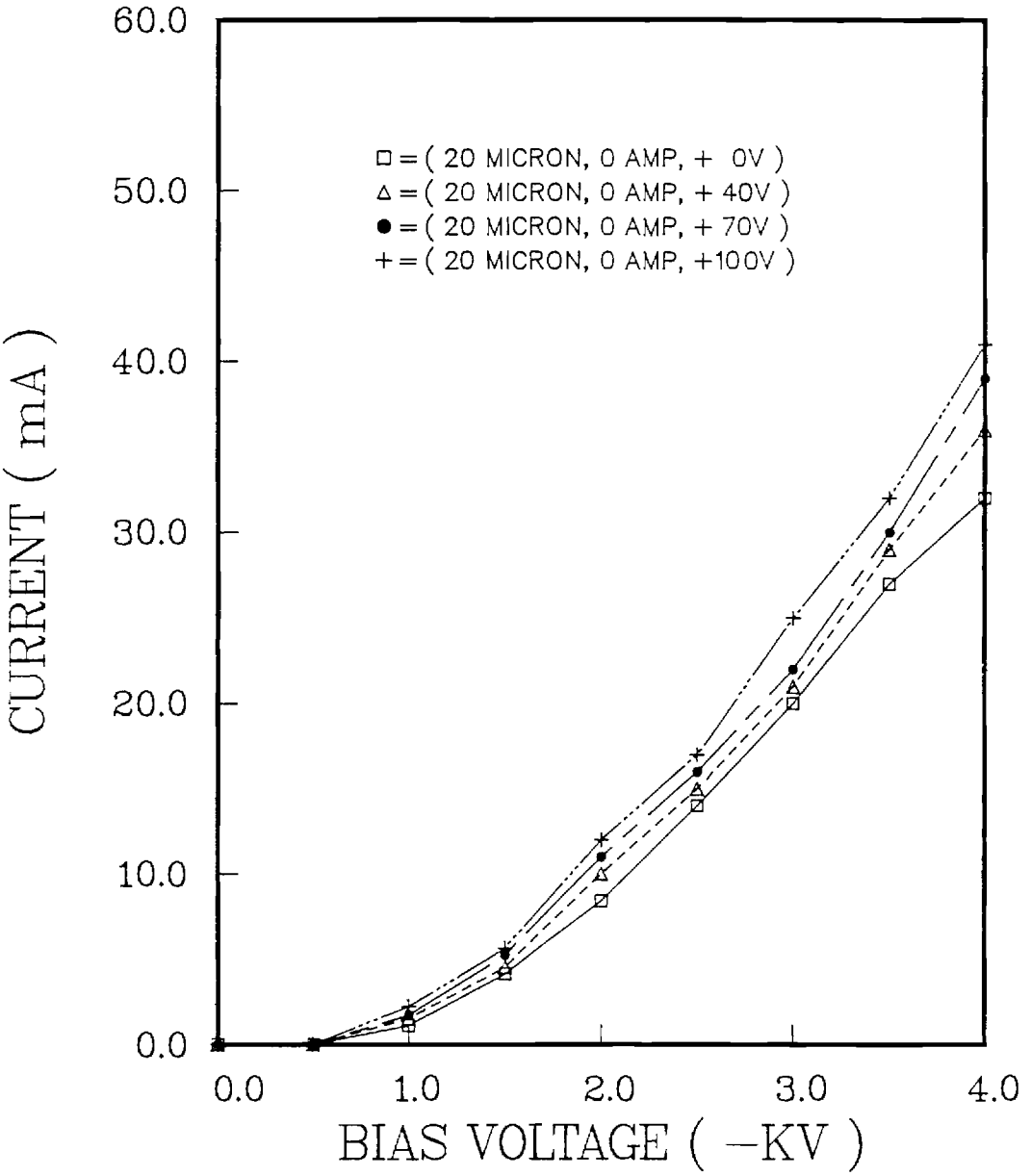

Figure 1. Current vs. Voltage Characteristic Curves of the Deposition System When It was Backfilled with 20 Microns of Argon. The Thermionic Filament was OFF.

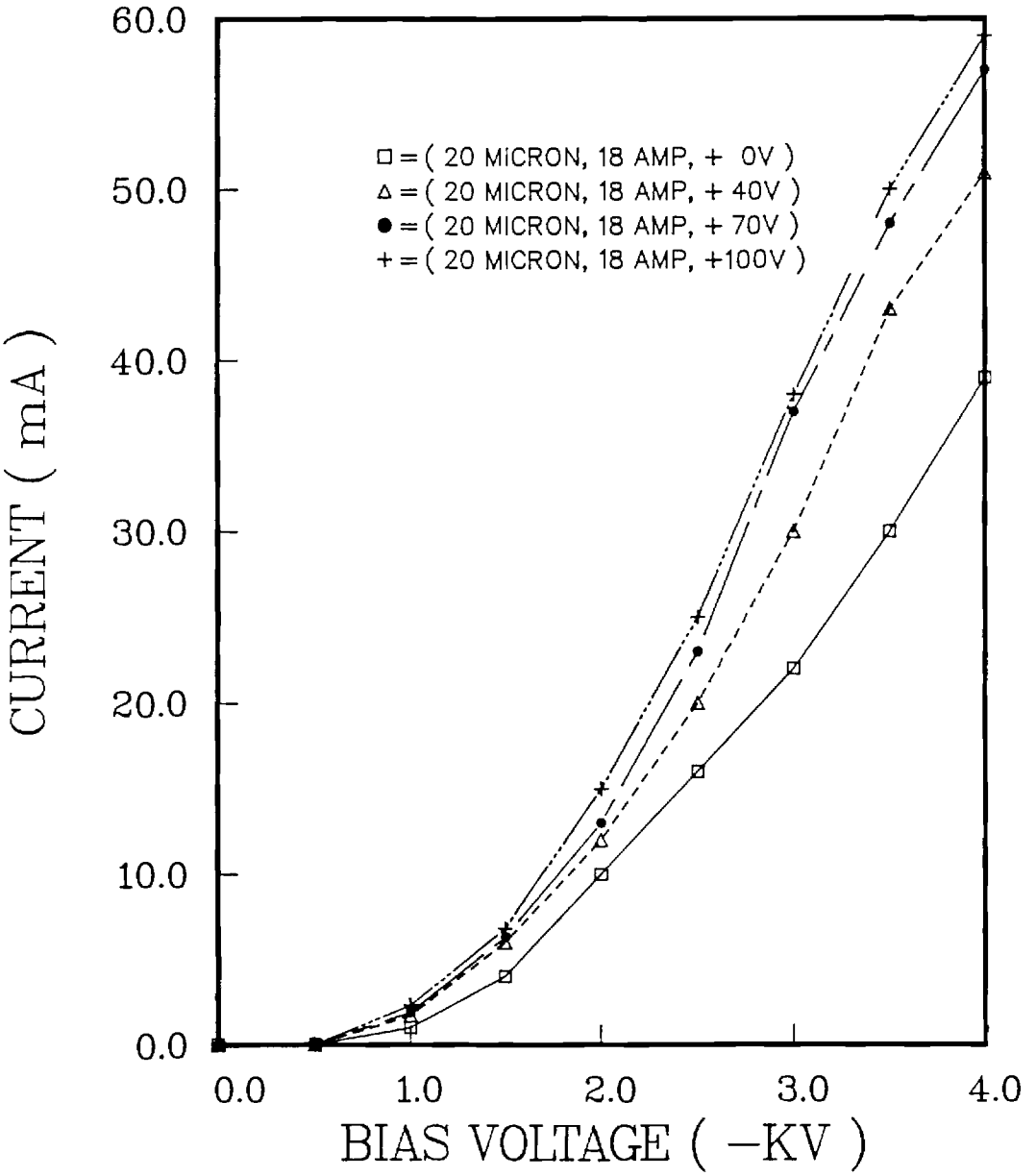

Figure 2. Current vs. Voltage Characteristic Curves of the Deposition System When It was Backfilled with 5 Microns of Argon. The Thermionic Filament was ON.

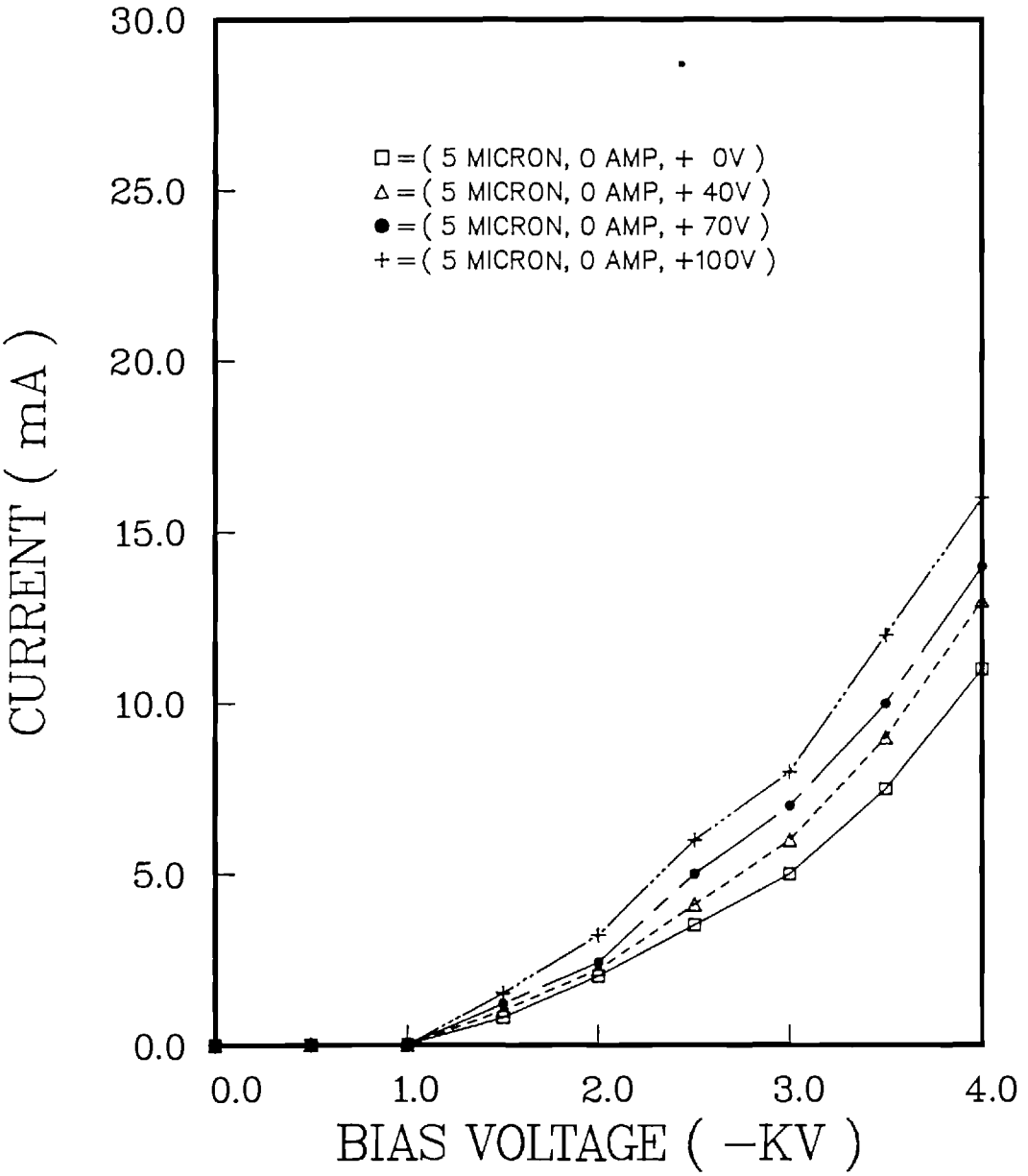

Figure 3. Current vs. Voltage Characteristic Curves of the Deposition System When It was Backfilled with 20 Microns of Argon. The Thermionic Filament was OFF.

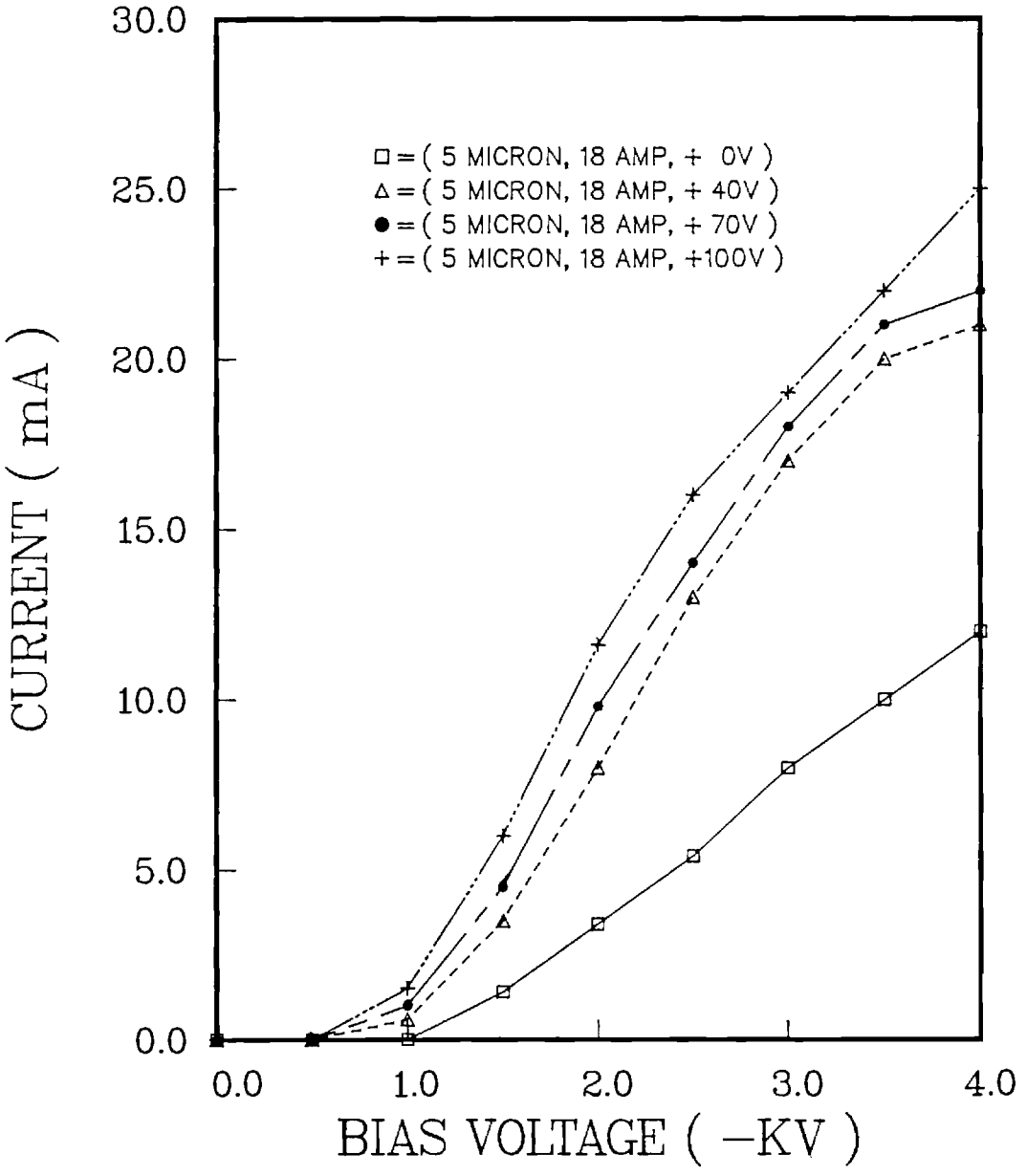

Figure 4. Current vs. Current Characteristic Curves of the Deposition System When It was Backfilled with 20 Microns of Argon. The Thermionic Filament was ON.

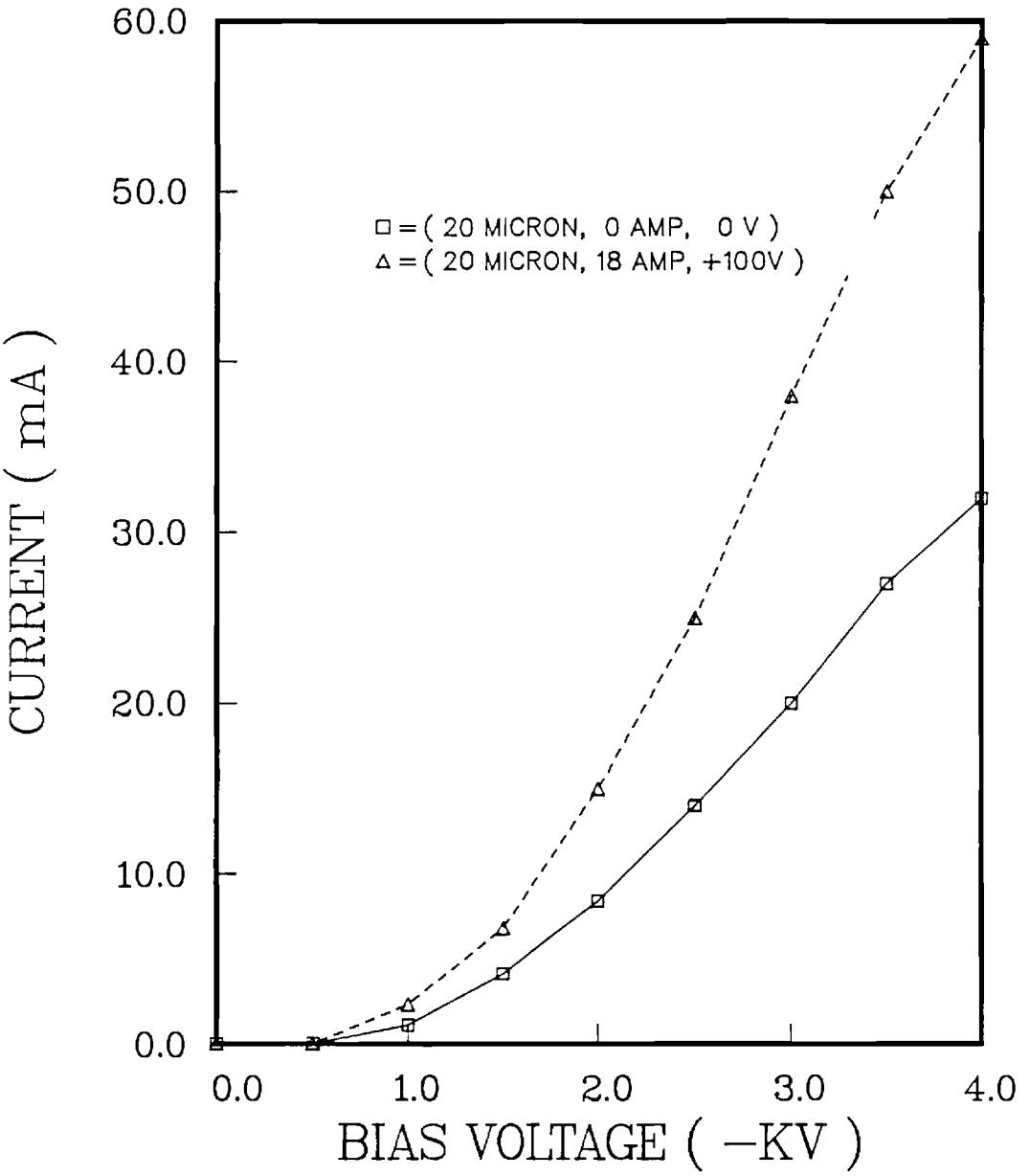

Figure 5. Comparison between Characteristic Curves for Diode Mode and Thermionically Assisted Triode Mode when the Argon Pressure was 20 Microns.

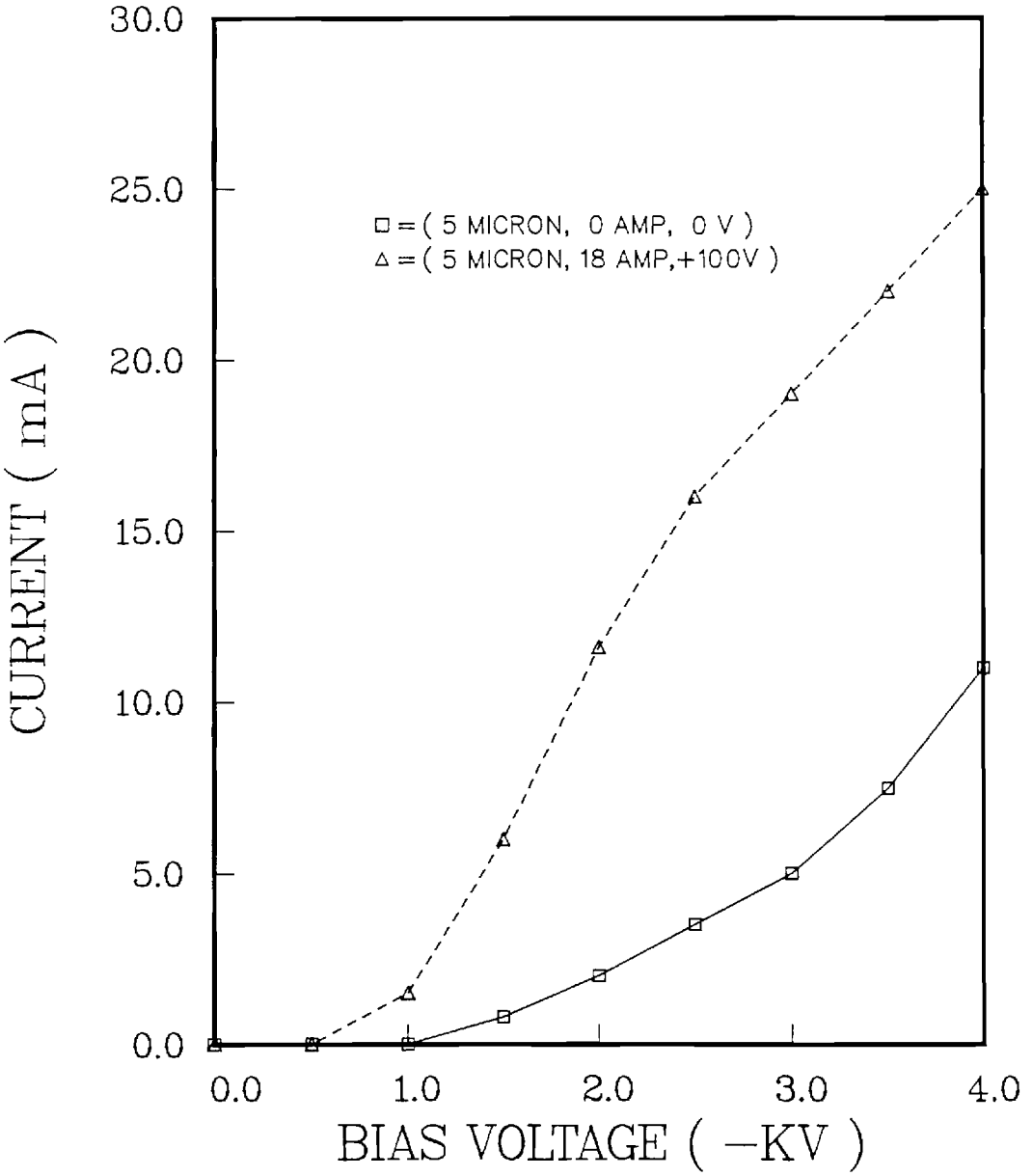

Figure 6. Comparison between Characteristic Curves for Diode Mode and Thermionically Assisted Triode Mode when the Argon Pressure was 5 Microns.

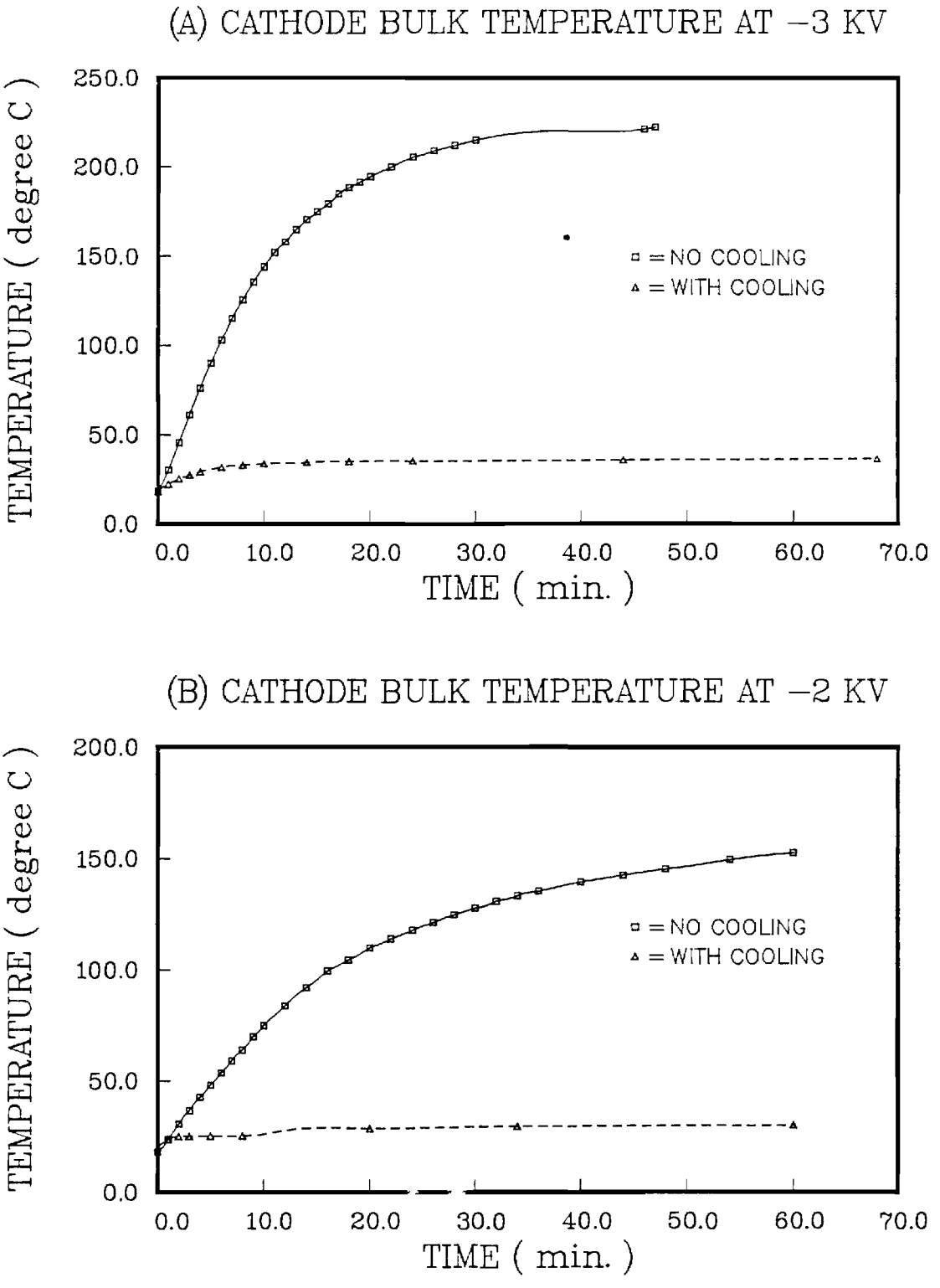

Figure 7. Variations of the Cathode Bulk Temperature at: (A) -3 KV, and (B) -2 KV during Sputter Cleaning With and Without Cooling.

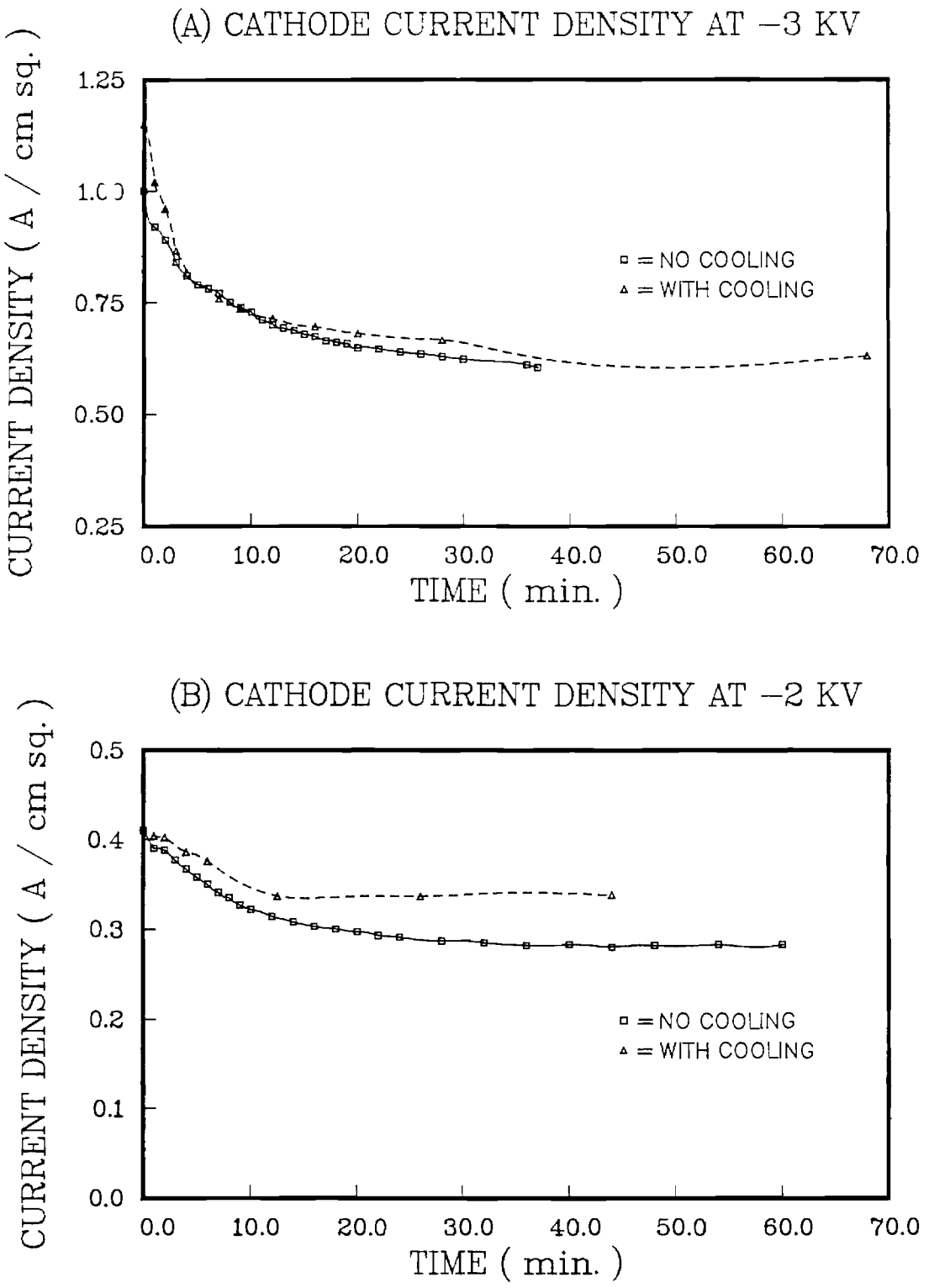

Figure 8. Variations of Cathode Current Densities at: (A) -3 KV, and (B) -2 KV During Sputter Cleaning With and Without Cooling.

E-18-6[illegible]

Georgia Tech

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March 21, 1989

MEMORANDUM REPORT

TO: Dr. E. J. Lee
IBM, Systems Technology Division Laboratory

FROM: Dr. Robert F. Hochman
Metallurgy Program
Georgia Institute of Technology

I. INTRODUCTION

As evidenced in the earlier work of this study, many variables effect the operation and characteristics of an ion plating system. Of these, the two that we feel most important are in themselves the result of several operational variables. These are the cleanliness of the system and the surface temperature of the substrate. The resultant film properties are very strongly dependent upon these characteristics. This has led us to look at such things as the total ionization efficiency as well as the cleanliness of the system itself. Most recently this led into the examination of the use of a thermionic assisted system whereby better control of ionization and improvement in cleanliness both appear possible. Therefore, this third in a series of reports in this study will deal with the evaluation of Cr film properties produced by thermionic assisted triode ion plating. Several interesting observations and conclusions with regards to the use of a thermionic emitter within an ion plating system will be presented.

II. EVALUATION OF FILM PROPERTIES FOR THERMIONIC ASSISTED TRIODE ION PLATED FILMS OF CHROMIUM

Contaminants in clean, well controlled diode and triode ion plating is still significant, especially at the film-substrate interface. In the case of A-3 (TATIP, +100 V), the oxygen content at the interface was measured at 6 percent and only trace amounts of carbon were detected. This is illustrated in Figures 1 and 2. The results of group A specimens reveal that, at 10 microns of argon pressure and -3 KV cathode bias, the contaminants in the glow discharge can be partially removed by using the TATIP technique.

In order to study the effect of cathode bias voltage in a TATIP system on the contamination of the coatings, Auger analysis was performed on group B specimens. The plots in Figures 3 and 4 show that when -2 KV was applied to specimen (B-3), the TATIP technique (+70 V probe bias with the thermionic filament supply on) under these conditions did not effectively reduce oxygen or carbon contaminants. However, when cathode bias is increased to -3 KV (A-2), less contaminants codeposit with the chromium. Further, if cathode bias is increased to -4 KV, the oxygen and carbon concentrations are below the detection limits of Auger spectroscopy, which are on the order of 0.1 atomic percent. These results are illustrated in Figures 5 and 6.

At 20 microns argon pressure, the chromium film on specimen D-1 produced by the DIP technique (-3 KV cathode bias) still contains oxygen (maximum concentration 8 %) and carbon as shown in Figures 7 and 8. Again, a peak was found in the carbon profile.

If a positive probe (biased at +70 V) and a hot filament are added to the coating system, the specimen (D-2) shows little oxygen contamination at the interface and its concentration in the bulk film is less than 1.0 %. These results are shown in Figures 9 and 10. When positive probe is biased at +100 V for specimen D-3, the oxygen concentration in the bulk film again is less than the detection limit of AES as shown in Figures 11 and 12.

Cooling of the substrate holder during ion plating, for both DIP and TATIP, does not have a significant effect on the concentration of the oxygen and carbon in the coating. On the other hand, cooling during vacuum evaporation experiments was shown to increase the amount of oxygen and carbon contamination in the chromium films.

It was interesting to observe that when a glow discharge is greatly enhanced a small carbon concentration peak is found at the interface. In order to understand the mechanism of carbon enrichment, a TATIP (cathode bias -3 KV, argon pressure 20 micron, probe bias +70 V) chromium coating was prepared on a pure Copper substrate. The Auger depth-profile of this film showed no carbon enrichment at the interface. This suggests that the carbon enrichment at interface can be attributed to the surface enhanced back diffusion of carbon from the M50 steel. Surface sputtering by energetic particles not only creates a large concentration of vacancies but also increases the surface temperature. The diffusion of carbon out of the M50 substrate is promoted and the formation of interface carbides occurs.

III. DISCUSSION OF TATIP FINDINGS

Two new findings of this work are to be discussed in this section. The first is the removal of contaminants from pure elemental coatings in an intensified glow discharge and the other is the carbon enrichment at the interface found for the high ionization efficiency conditions and a steel substrate.

For low ionization efficiency experiments, it was found that a high concentration of oxygen was uniformly distributed throughout the chromium coating. Carbon was also detected although in lower concentrations. The source of these contaminants is believed to be from typical vacuum system leaks and the backstreaming of diffusion pump vapor into the chamber. The DIP technique can not avoid oxygen and carbon contamination in the early stages of film formation. However, increasing the ionization efficiency by using the TATIP technique can greatly reduce the concentration of these contaminants. A calculation, following the procedure suggested by Physical Electronics Industries, Inc., shows that the concentration of these contaminants is essentially below the Auger detectability limit, which in the test conditions used for this experiment, was 0.1 % a/o.

A simple model is proposed to explain the effect of increased ionization efficiency on contamination reduction. When a TATIP system is energized, a large number of thermionic electrons are emitted into the plasma and are attracted by the positive probe. The contaminants suffer more ionizing collisions because more ionized and energetic particles are available in the system.

Negatively ionized contaminants are attracted by the positive probe or deposited on ground chamber walls. The 'electrical pumping' effect of contaminants is improved when the ionization efficiency is increased.

No significant difference in contaminant concentration was detected between cooled and noncooled ion plated films. This is due to the preferential sputtering of oxygen from the surface. For the straight vacuum evaporation experiments, contamination concentration in the cooled specimen is about 2.5 times of that in noncooled specimen. This results because the cooled surfaces are favorable for gas adsorption.

Carbon enrichment at the interface was found in the very high ionization efficiency experiments. Careful study of the individual signal for carbon shows an increase from 10 to 15 % in peak-to-peak intensity may be detected at the interface. In order to ascertain that the carbon enrichment observed does not come from contamination an AES depth profile was performed on chromium coated (DIP and TATIP) copper specimens. Results shown in Figures 13 and 14 reveal that on a CR/CU DIP film carbon contamination does exist at the interface, however, no carbon is detected at the interface of CR/CU for the TATIP film. These results confirm our hypothesis that the carbon enrichment at the interface of CR/M50 TATIP films does not come from environment, but from carbon back diffusion from the steel substrate matrix.

IV. OBSERVATIONS AND CONCLUSIONS BASED ON TATIP STUDIES

A. The use of a thermionic filament and a positive probe can

enhance the ionization efficiency of the plasma by a factor of 2.9 under the conditions tested. The increased energy and number of particles bombarding the cathode are suggested to be responsible for the improved properties of the films.

B. The morphology of thin chromium films can be greatly improved by using the thermionically assisted triode ion plating technique. When the ionization efficiency in the glow discharge is increased, the columnar structures observed in vacuum evaporated and diode ion plated chromium films are completely eliminated in TATIP films. This is related to the favorable effect of the increased number and energy of energetic particles bombarding substrate surface.

C. The contamination of the pure chromium coating by either oxygen or carbon can be essentially eliminated by using TATIP technique. This may be attributed to the attraction by the probe for negative contaminant ions.

D. Carbon enrichment at the film-substrate interface is detected in high ionization efficiency TATIP films presumably because more energetic chromium ions/atoms can overcome the energy barrier for reaction with the carbon which diffuses out of substrate.

E. The corrosion resistance of the chromium coatings in deaerated 0.1 M NaCl solutions increases with increased ionization efficiency during deposition. This is mainly

due to the improved film morphology achieved with the enhanced ionization.

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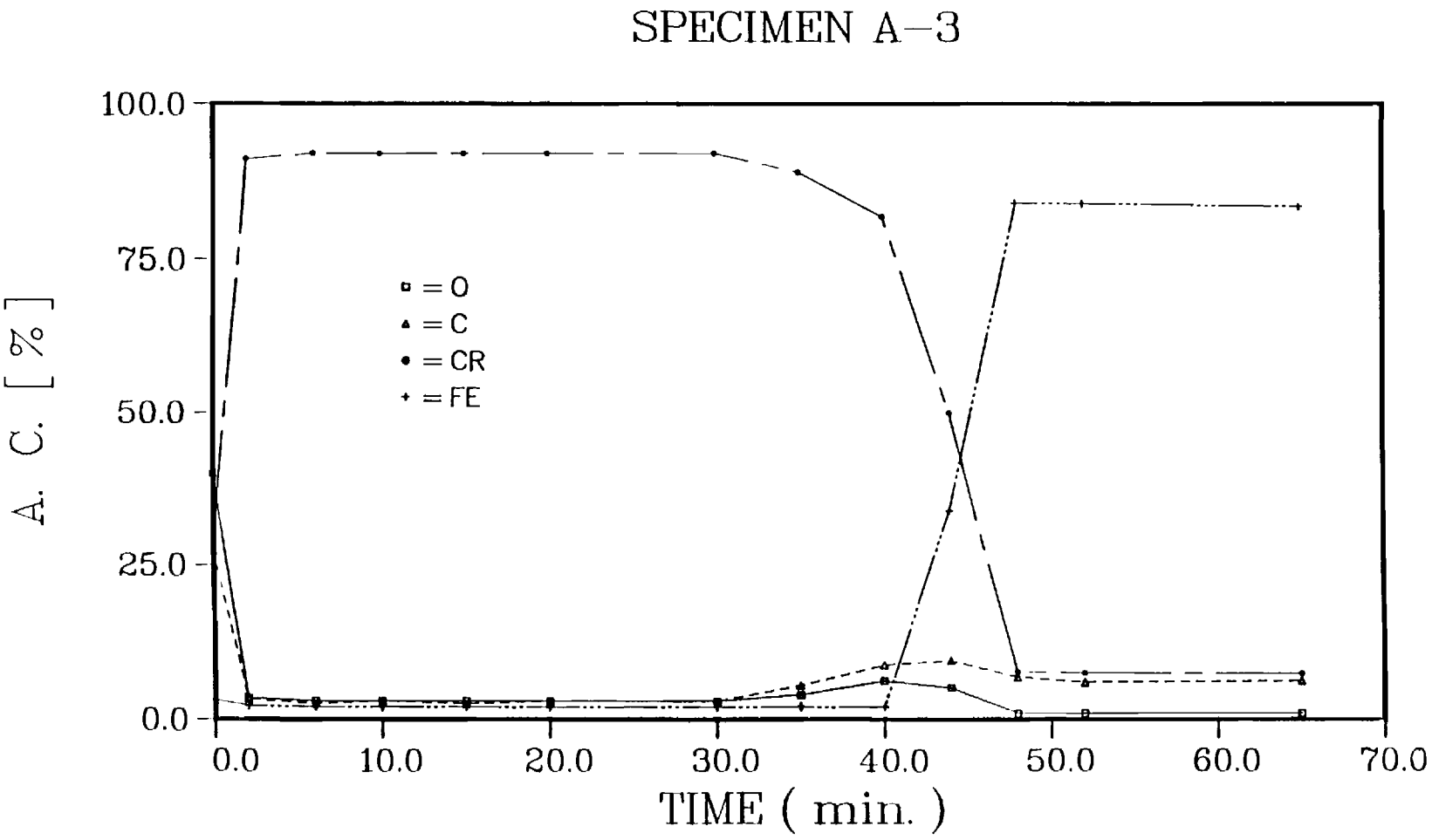

Figure 1. The Auger Depth Profile of Specimen A-3 (TATIP, Cathode Bias -3 Kv, Argon Pressure 10 Microns, Probe Bias +120 V).

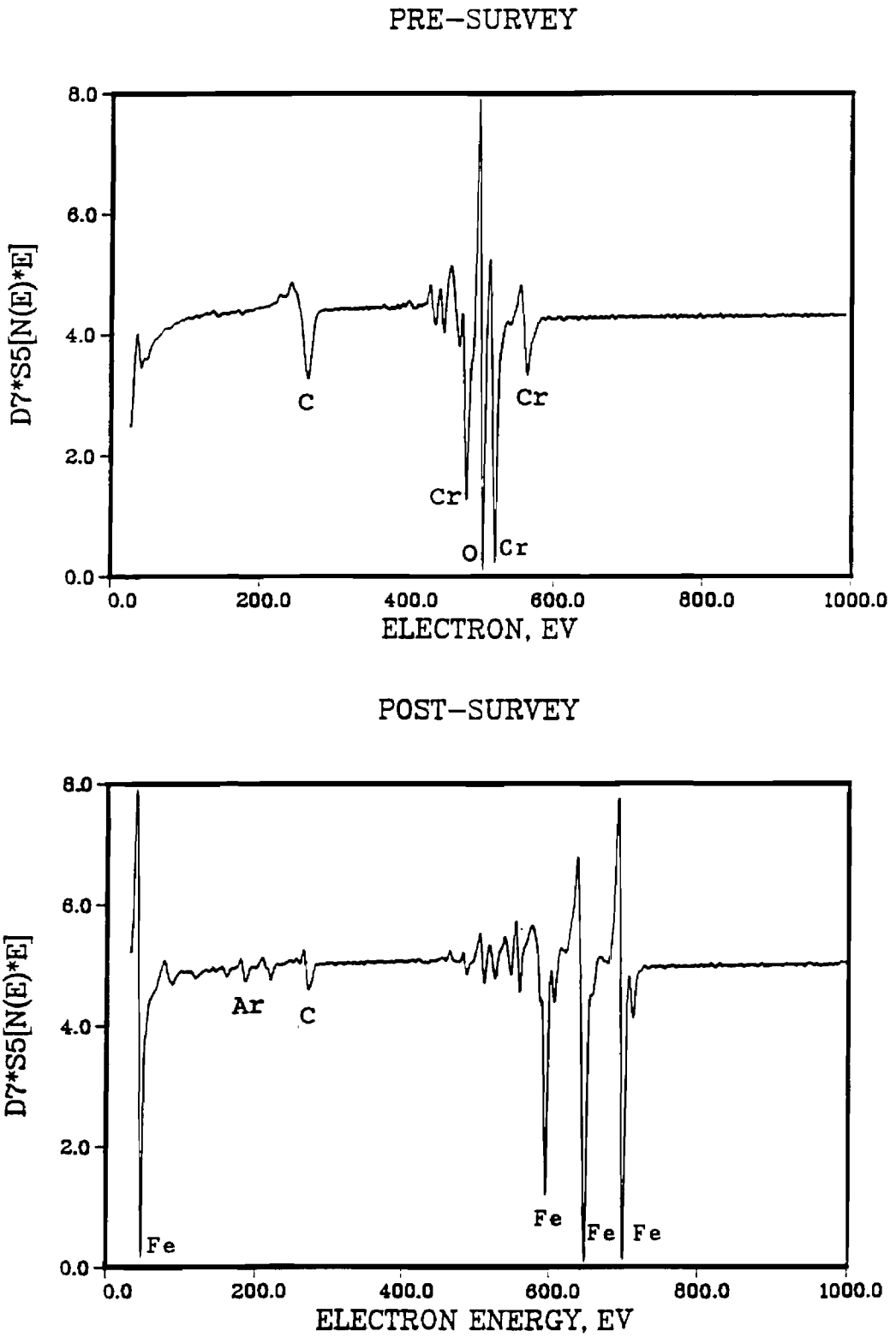

Figure 2. Differentiated Auger Electron Spectra from Specimen A-3: (1) Before and (2) After Depth Profile Analysis.

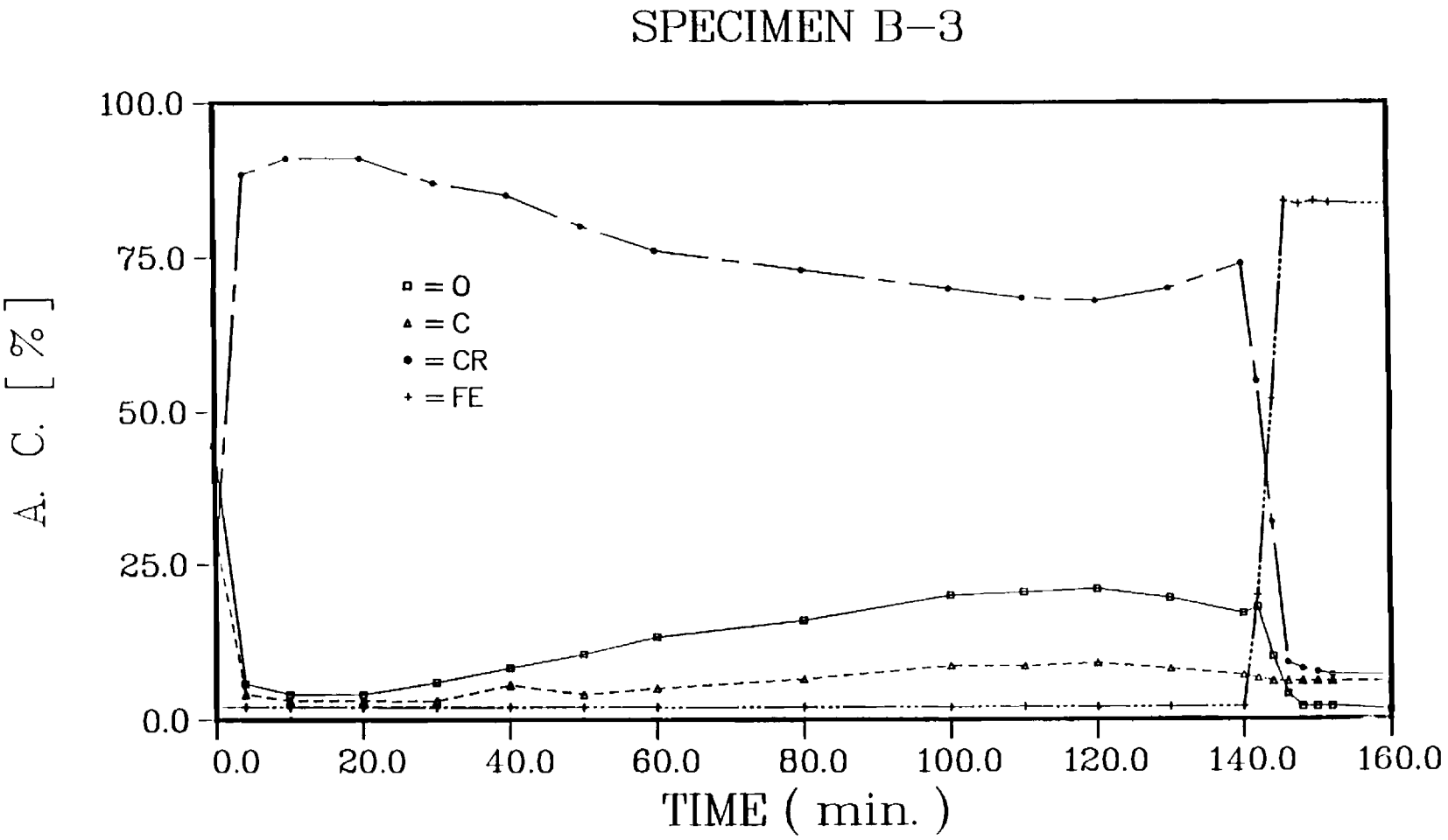

Figure 3. The Auger Depth Profile of Specimen B-3 (TATIP, Cathode Bias -2 Kv, Argon Pressure 10 Microns, Probe Bias +70 V).

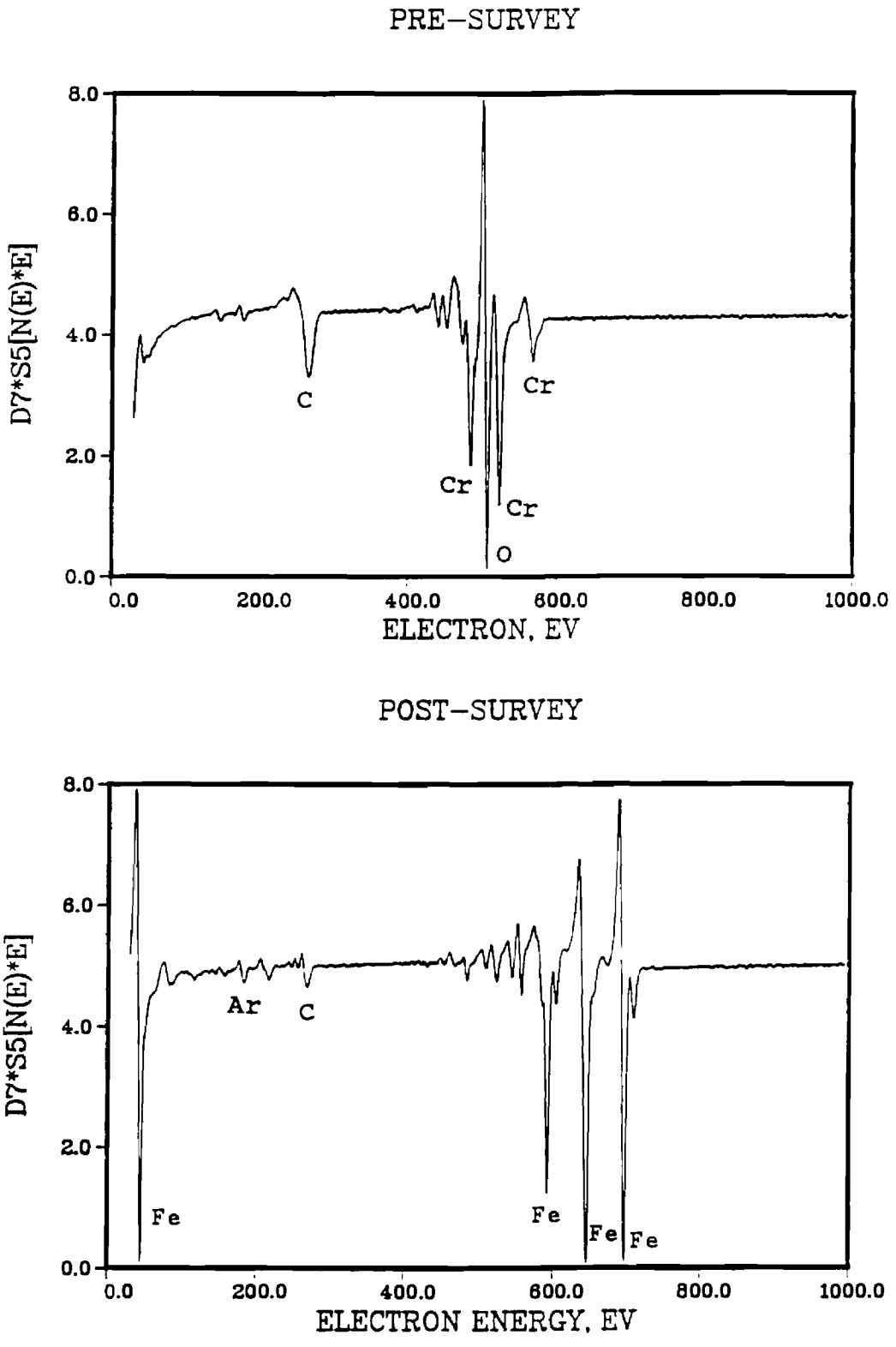

Figure 4. The Differentiated Auger Electron Spectra from Specimen B-3: (1) Before and (2) After Depth Profile Analysis.

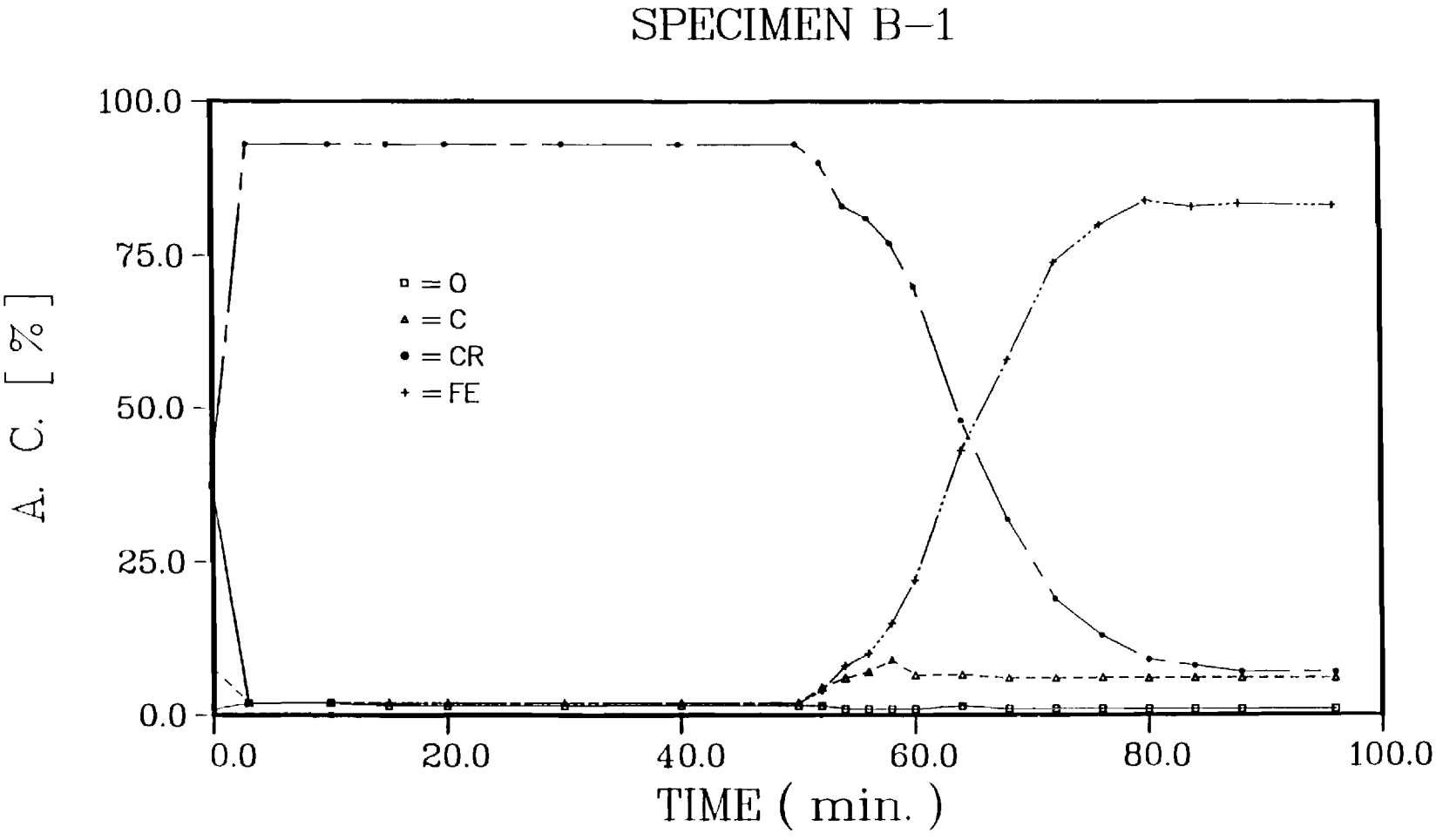

Figure 5. The Auger Depth Profile of Specimen B-1 (TATIP, Cathode Bias -4 Kv, Argon Pressure 10 Microns, Probe Bias +70 V).

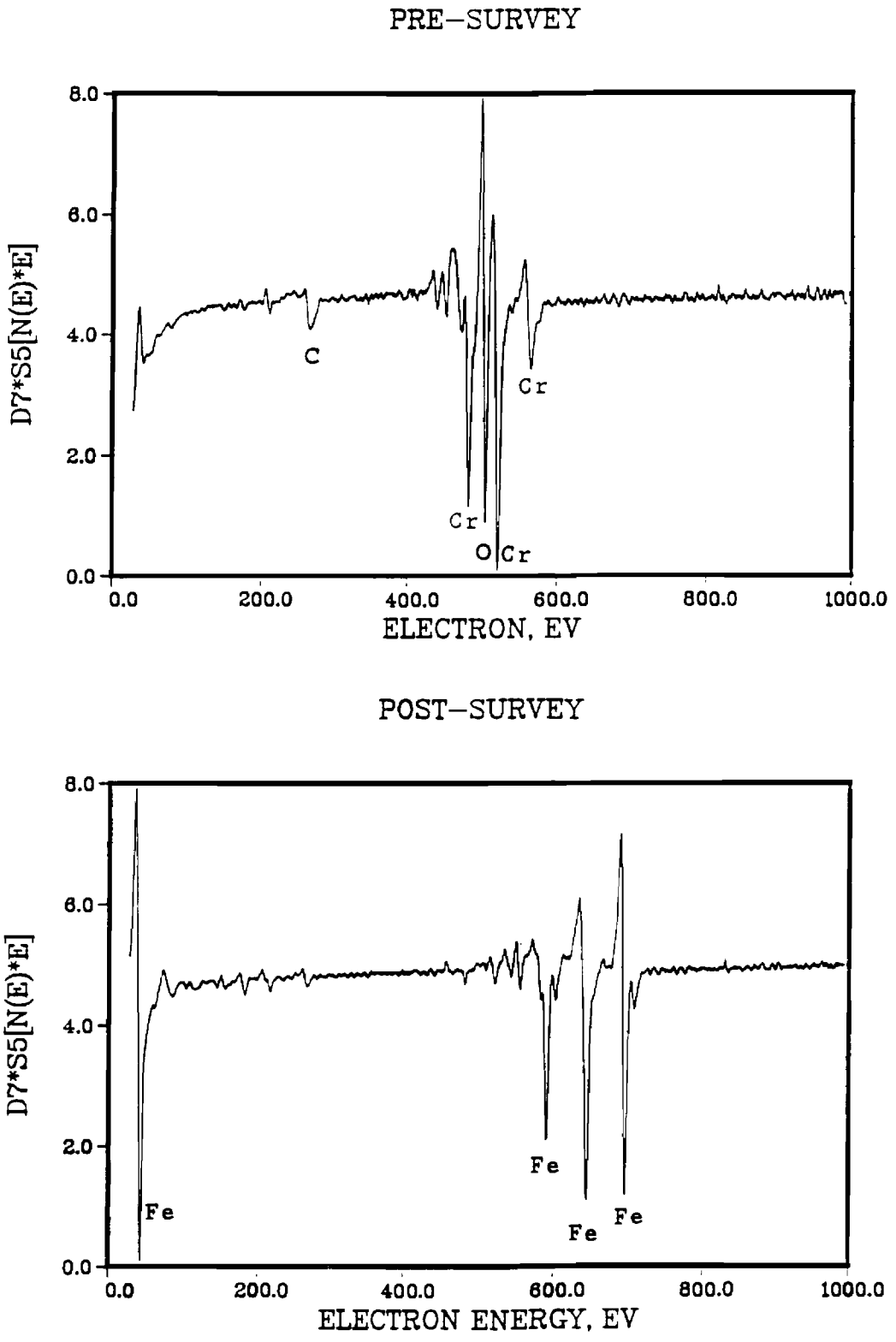

Figure 6. The Differentiated Auger Electron Spectra from Specimen B-1: (1) Before and (2) After Depth Profile Analysis.

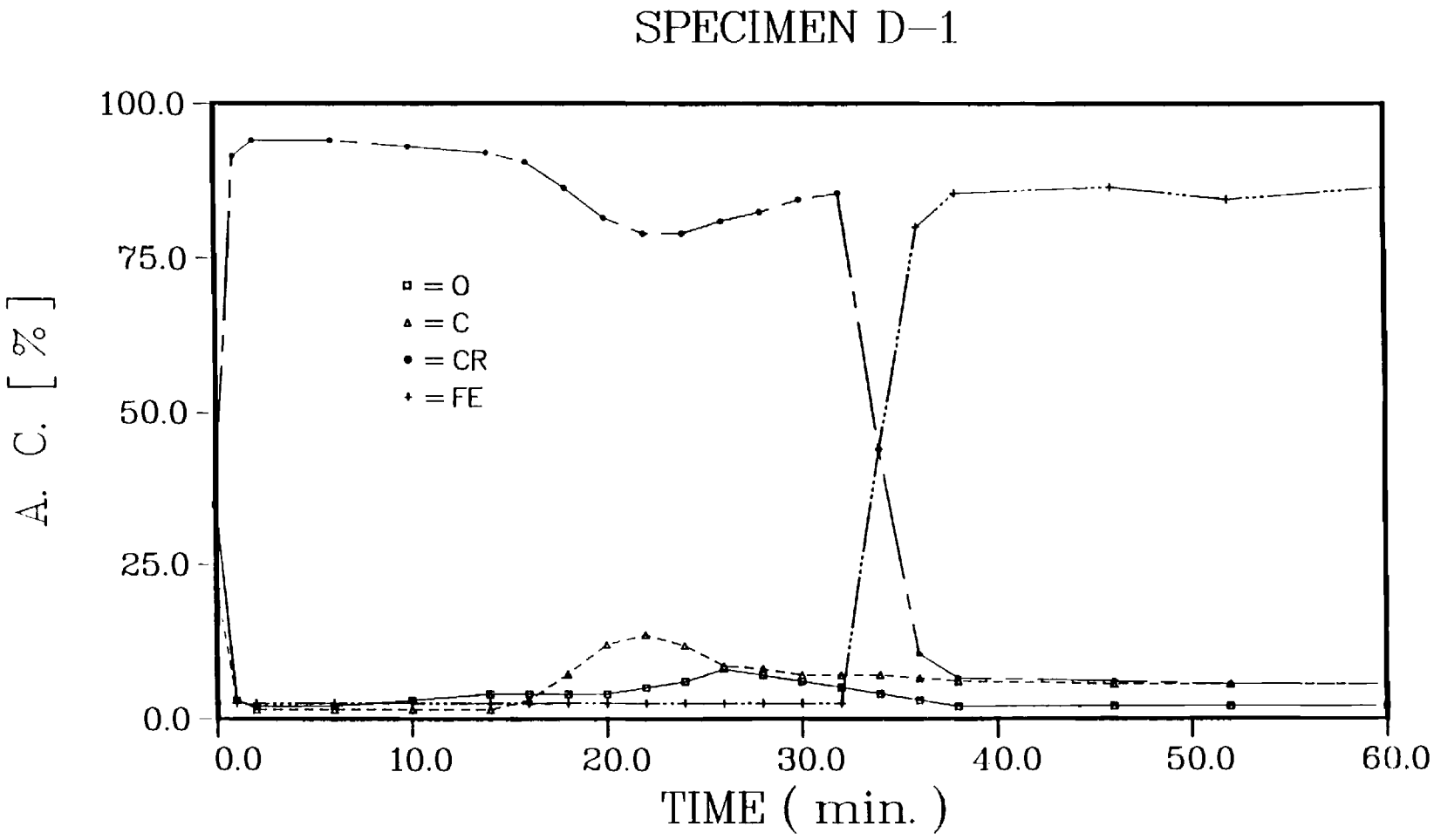

Figure 7. An Auger Depth Profile of Specimen D-1 (DIP, Cathode Bias -3 Kv, Argon Pressure 20 Microns).

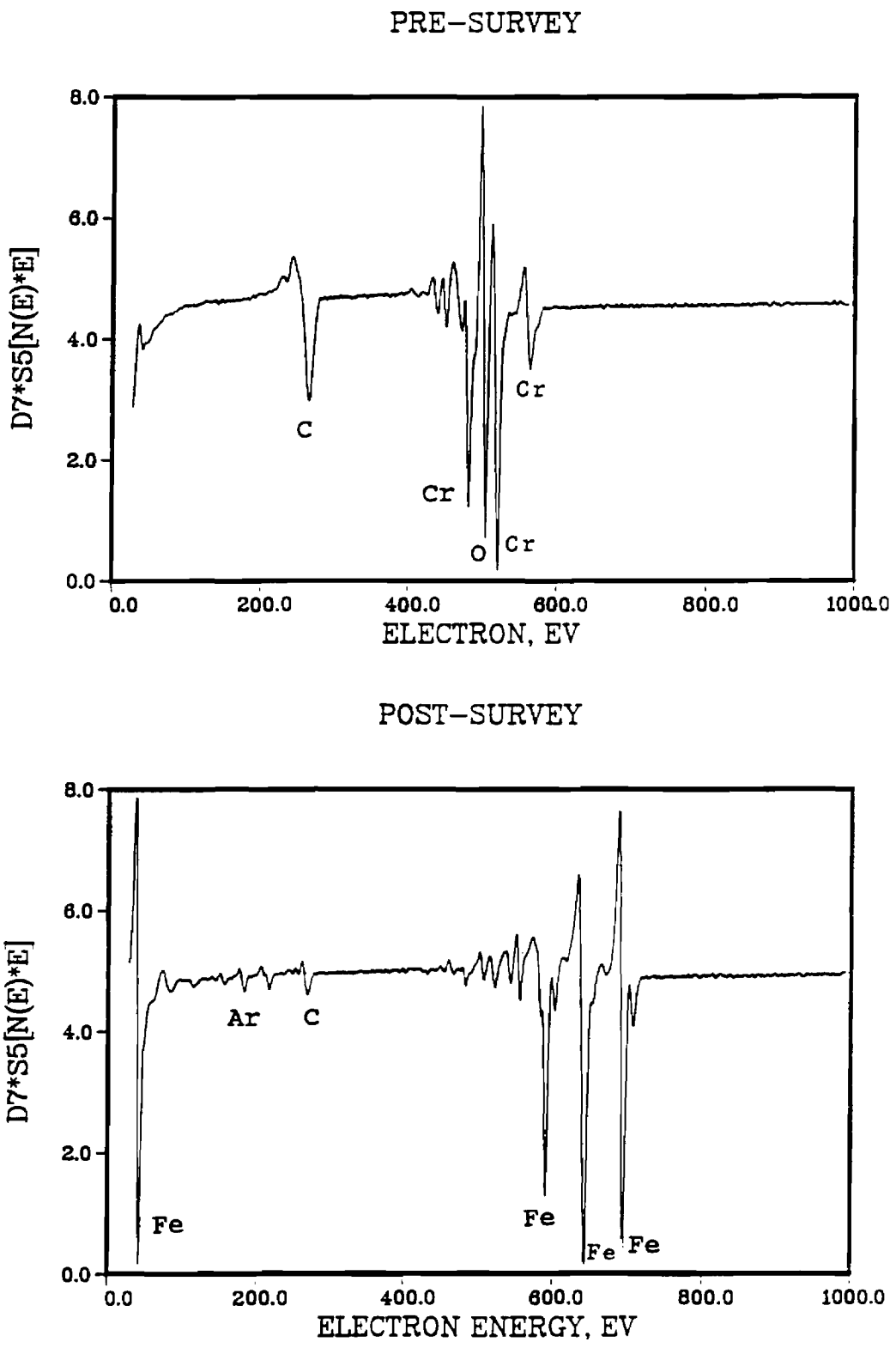

Figure 8. A Differentiated Auger Electron Spectra from Specimen D-1: (1) Before and (2) After Depth Profile Analysis.

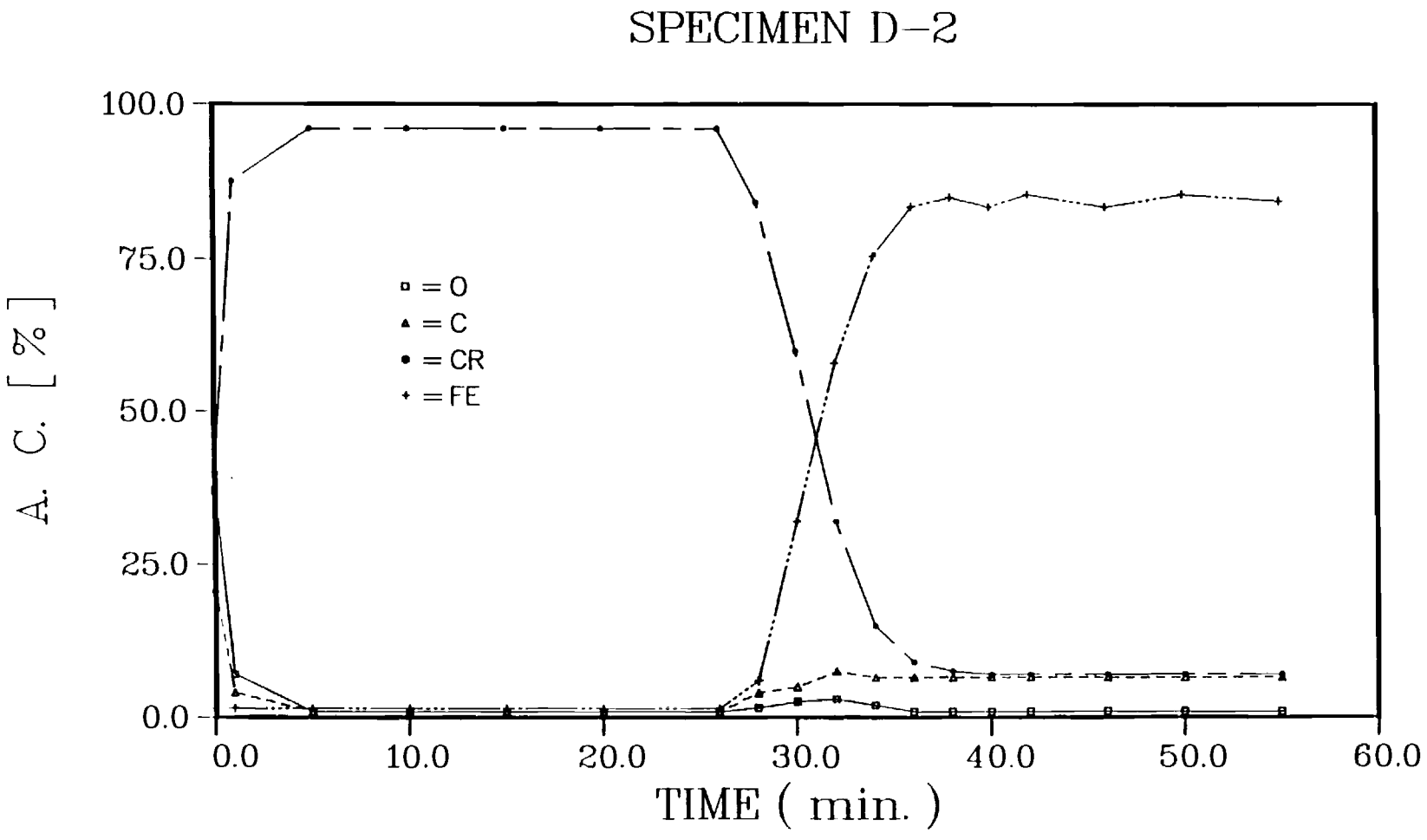

Figure 9. The Auger Depth Profile of Specimen D-2 (TATIP, Cathode Bias -3 Kv, Argon Pressure 20 Microns, Probe Bias +70 V).

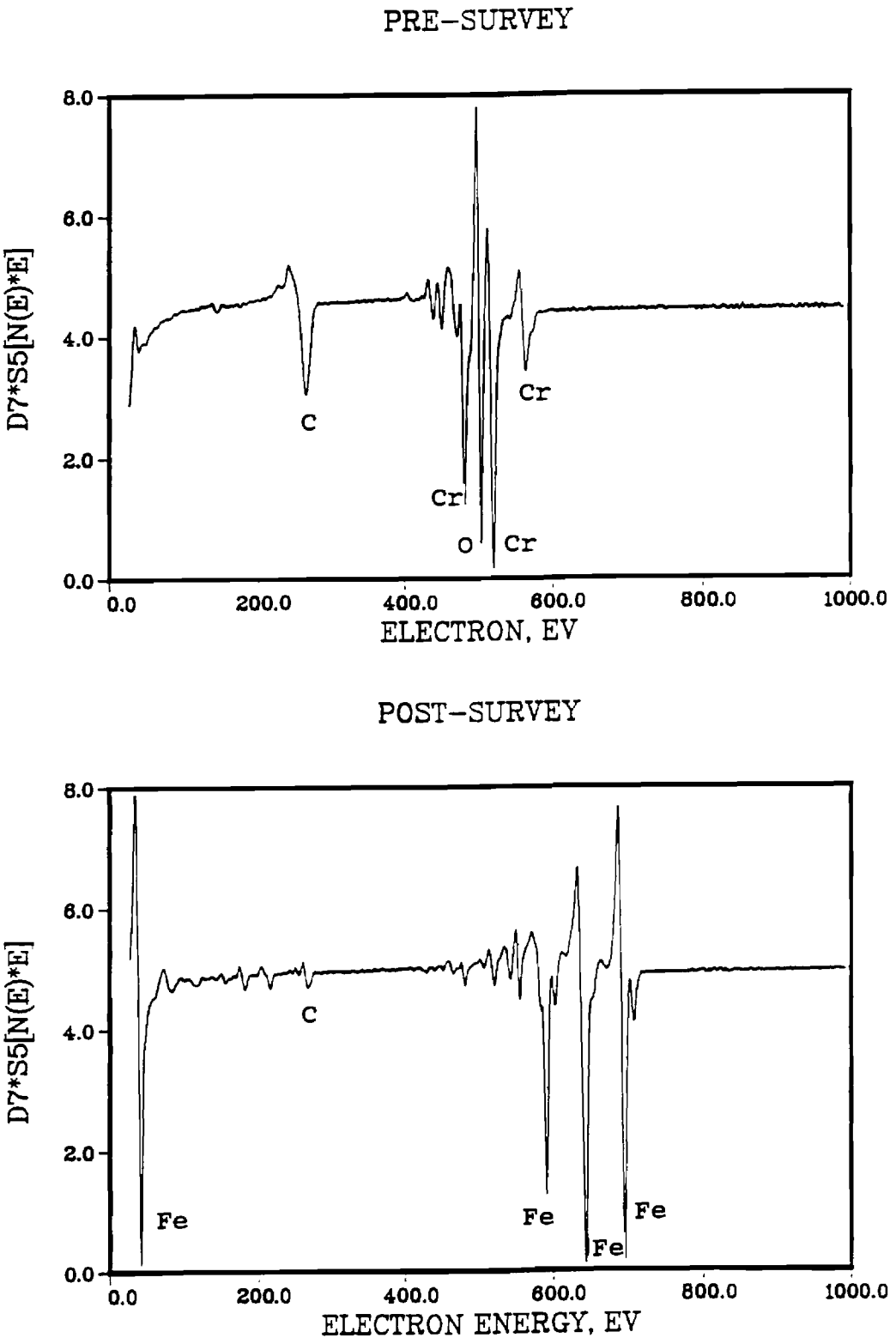

Figure 10. The Differentiated Auger Electron Spectra from Specimen D-2: (1) Before and (2) After Depth Profile Analysis.

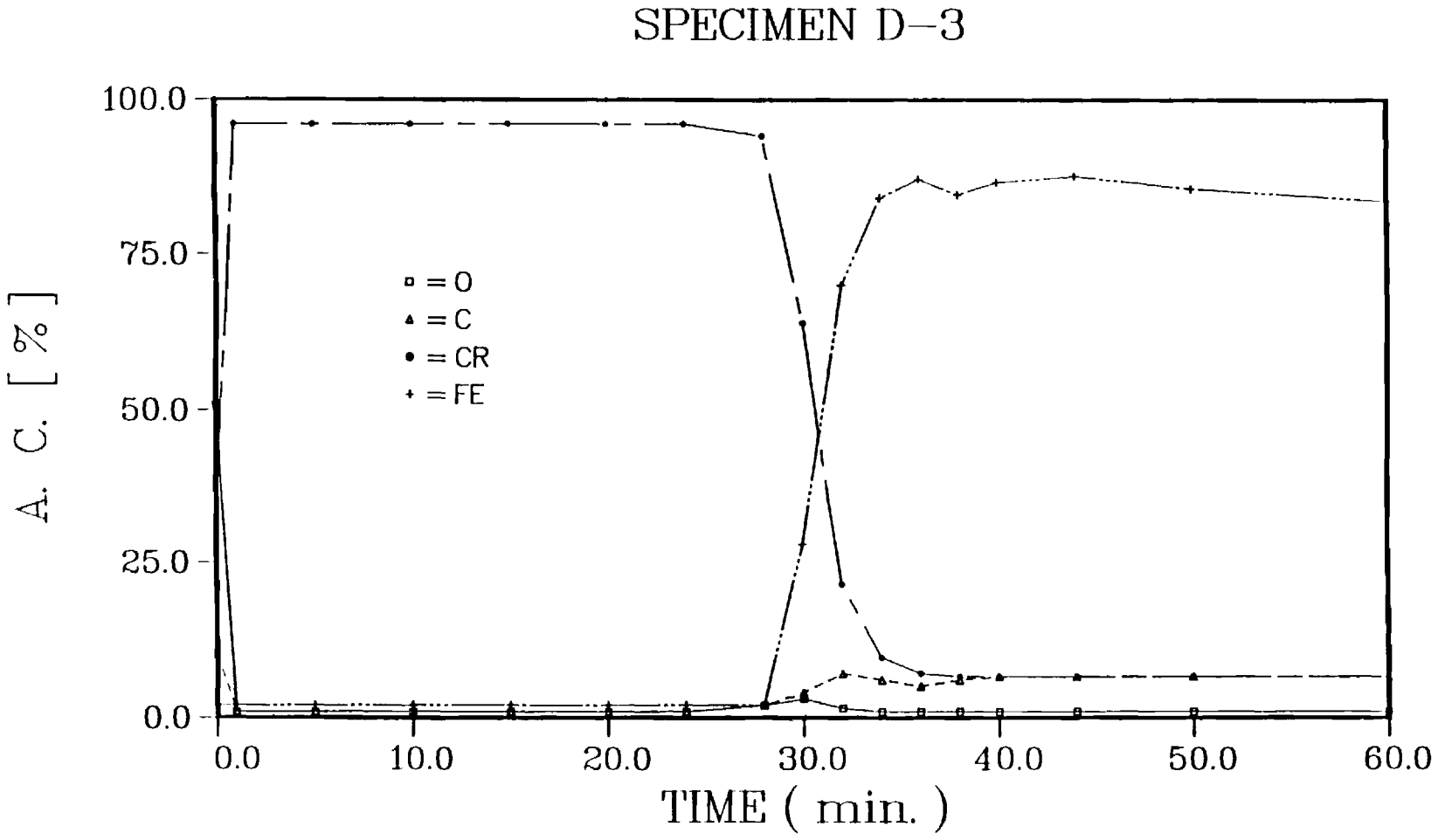

Figure 11. The Auger Depth Profile of Specimen D-3 (TATIP, Cathode Bias -3 Kv, Argon Pressure 20 Microns, Probe Bias +100 V).

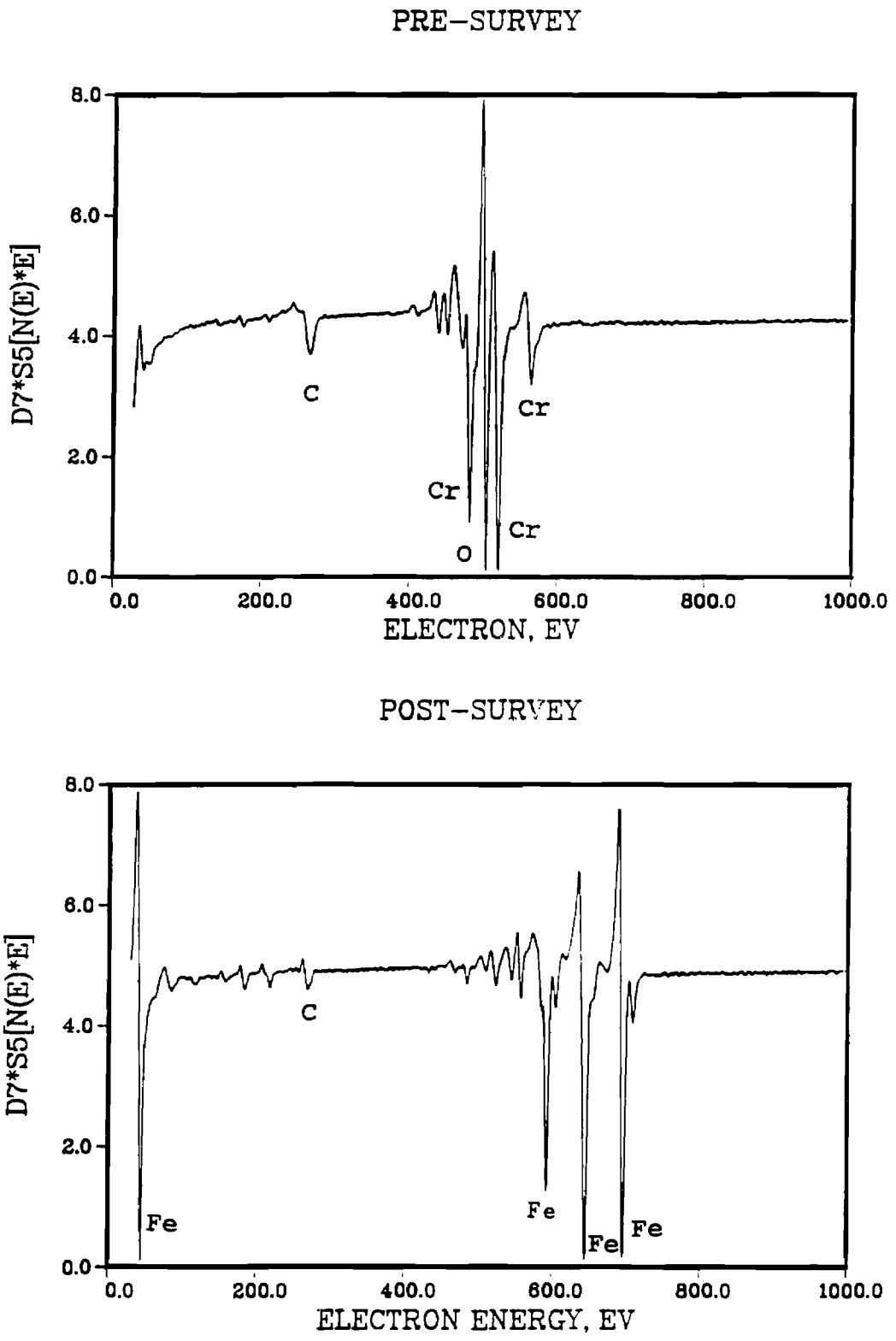

Figure 12. The Differentiated Auger Electron Spectra from Specimen D-3: (1) Before and (2) After Depth Profile Analysis.

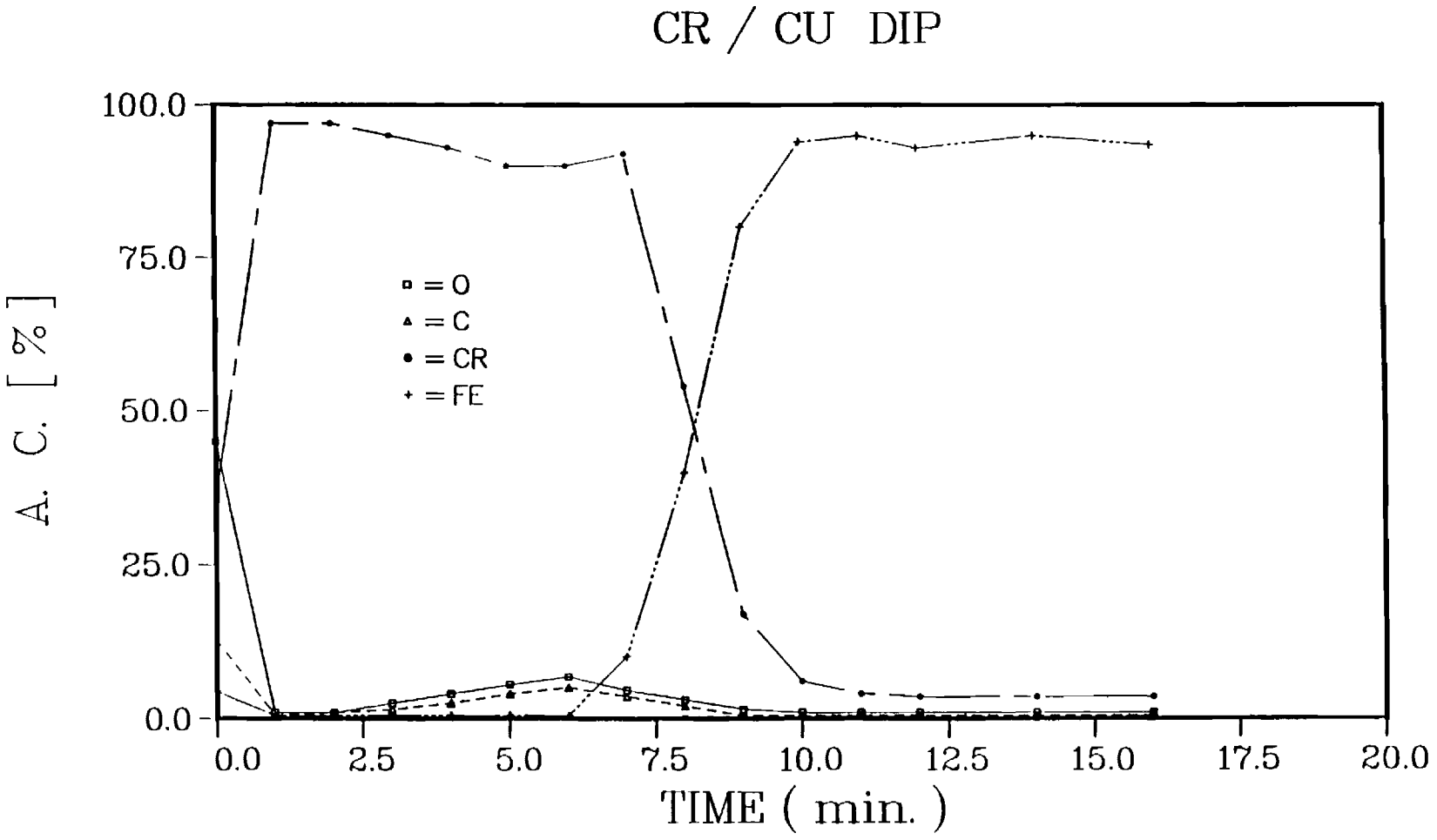

Figure 13. The Auger Depth Profile of Specimen CR/CU (DIP, Cathode Bias -3 Kv, Argon Pressure 20 Microns, Water Cooling).

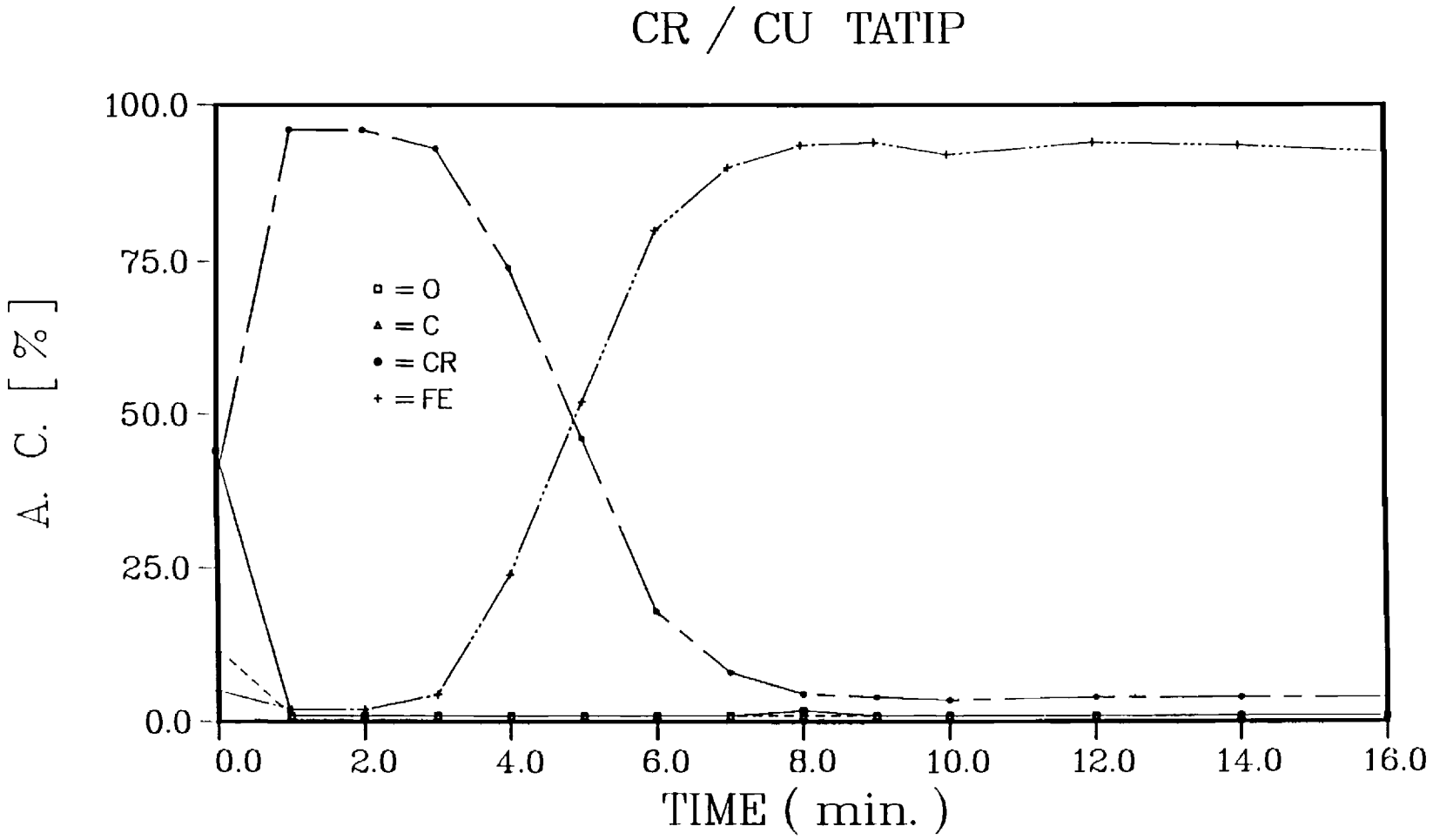

Figure 14. The Auger Depth Profile of Specimen CR/CU (TATIP, Cathode Bias -3 Kv, Argon Pressure 20 Microns, Water Cooling).